This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

Chem 668.70.2

Harvard College Library

FROM

The Harvard Medical
School

SCIENCE CENTER LIBRARY

Pa 1799

A MANUAL

OF

QUALITATIVE ANALYSIS.

A MANUAL

OF

QUALITATIVE ANALYSIS.

John Bryant

BY

ROBERT GALLOWAY, F.C.S.,

PROFESSOR OF APPLIED CHEMISTRY IN THE ROYAL COLLEGE OF SCIENCE FOR IRELAND, AUTHOR OF 'THE SECOND STEP IN CHEMISTRY,' 'THE FIRST STEP IN CHEMISTRY,' ETC.

FIFTH EDITION.

Rewritten and Enlarged. With Plate and other Illustrations.

LONDON:
JOHN CHURCHILL AND SONS, NEW BURLINGTON STREET.

MDCCCLXX.

Chem 668.70.2

HARVARD COLLEGE
APR 1909
LIBRARY.

From the
Harvard Medical School

PRINTED BY
J. E. ADLARD, BARTHOLOMEW CLOSE

PREFACE

TO THE

FIFTH EDITION.

THIS Edition contains numerous and important additions, and some alterations have been made in the arrangement of the different divisions of the book; but the plan or scheme of analysis which formed the foundation of the First Edition, and which is explained in the Preface to the Second and in the Introduction to the present one, remains unchanged, and is the foundation of the present as it was of all the previous Editions. I have continued it, not simply because other teachers, as well as myself, prefer it to the system of Fresenius or that of the Giessen outlines, having found it more successful, especially with students who can only devote a portion of their time to the study of analytical chemistry, but because I believe it to be in accordance with the laws of thought. (1) It exhibits a like progression to the mind; it begins with a few subjects and successively adds to them until the entire system is reached; it proceeds, in short, from the simple to the complex. (2) The Tables are not constructed on the bad system of the Giessen outlines and some other analytical works, or on the system of Fresenius, which is quite as faulty, and still more unpractical for the learner—of *telling* this and *showing* that, making the learner a mere recipient—but on the better system of making the student *compare, distinguish, judge;* so that thus, instead of being a recipient, he may become an intelligent and active discoverer. In addition to the methods developed in the Tables for separating the members of the different groups, others are given in this Edition which the student ought to practise as soon as he can examine substances correctly by the methods given in the Tables.

The old system of teaching Practical Chemistry had some advantages over the method now generally in use. I have endeavoured in the present Edition to remove the defects of the present system by describing very fully the properties of the metals, their oxides and chief salts, in order that the student may carry on with the study of analysis other experimental inquiries, either by preparing substances or by studying other than the analytical properties of bodies.

I have given at the end of each group and important division of the book a series of examination questions in Practical Chemistry; many of them, so far as I am aware, are of an *entirely new character*, and these have been framed, not for testing the memory, which is the only faculty of the mind exercised by the questions usually given at chemical examinations, but for ascertaining whether the student has so studied the science that he is capable of reasoning upon it. Owing to memory-questions forming the bulk of the questions usually given at chemical examinations, it has become no uncommon practice with those who are going in for examination, to commit to memory some one of the smaller text books on the science, or the pet subjects of the examiner.

As the new class of questions I have given cannot be answered by the cramming process, I believe they will ultimately be as generally adopted as what are termed the 'arithmetical questions,' which I was the first to introduce in my 'First Step in Chemistry.'

In the portion of the work more immediately devoted to analysis the following are *some of the additions* which have been made:—1st. Bunsen's flame reactions have been given, with a plate of figures of the apparatus. 2nd. The detection of the poisonous metals and acid-radicals in the presence of organic matter. 3rd. Additional tests for the detection of the individual alkaloids, and more complete systematic methods for the detection of these bodies.

The new notation has been adopted; and the division of the book into three chief parts, and the arrangement of these parts, will, I hope, be found to be an improvement.

In conclusion, allow me to direct the student's attention to the following extract from Thomas Carlyle's 'Address to the Students of the University of Edinburgh:'—"By diligence I mean among other things—and very chiefly—honesty in all your inquiries. Pursue your studies in the way your conscience calls honest. More and more endeavour to do that. Keep, I mean to say, an accurate separation of what you have really come to know in your own minds, and what is still unknown. Be careful not to stamp a thing as known when you do not yet know it. Count a thing known only when it is stamped on your mind, so that you may survey it on all sides with intelligence. There is such a thing as a man endeavouring to persuade himself, and endeavouring to persuade others, that he knows about things when he does not know more than the outside skin of them, and he goes flourishing about with them. There is also a process called cramming in some universities—that is, getting up such points of things as the examiner is likely to put questions about. Avoid all that; it is entirely unworthy of an honorable habit. Gradually see what kind of work you can do; for it is the first of all problems for a man to find out what kind of work he is to do in this universe. In fact, morality as regards study is, as in all other things, the primary consideration, and overrides all others. A dishonest man cannot do anything real. . . . . He does nothing but darken counsel by the words he utters."

ROBERT GALLOWAY.

December, 1869.

PREFACE

TO THE

SECOND EDITION.

In issuing a New Edition of this Manual, I will here briefly describe the scheme or plan of analysis developed in the Work, and the way in which the book ought to be used.

In all other works on Qualitative Analysis with which I am acquainted, the properties of the bases and acids, and the application of these properties to the analysis of substances, are treated separately. As a consequence, the student, when he goes through the experiments on each base and acid, performs these illustrations of the properties without perceiving their use or application. In the part of the Work devoted to the analytical course, he is *told what to do* either by tables (as in the 'Giessen Outlines,' and some other works), or, as in Fresenius, by a more tedious and, in my opinion, as defective a method. The principles upon which these instructions are based are not given with the instructions, but in a separate chapter of the Work; and unless the student is able himself to unite the two—the principles with the practical instruction—he becomes a mere analytical machine. Students who can give their whole time and attention to the study of the science can, if they will, accomplish this; but I have found by experience that those who can only devote some five or six hours in the week to the acquirement of the science fail to become intelligent analysts by this system.

The system is very difficult, as well as defective; it is so difficult that those who employ it generally teach one thing, useless in itself, in order that they may teach another; they teach the student first to look for one acid and one base—a limitation which is not adopted in actual practice—solely for the purpose of rendering the course in which they have to look for all the bases and acids less difficult.

In the plan I have adopted the properties of the different members of each group are contrasted by placing them in parallel columns; the advantage of this is, that the student, after he has performed the experiments, is able himself to devise methods for the detection and separation of the different members; it places him, in fact, in the position of a judge who has to decide some cause after having heard all the pleadings. It enables him also to judge for himself how many different methods might be adopted in the separation of substances; it therefore enlarges his views, and enables him to *reason* on the methods he adopts.

This Manual is intended to be used in the following way:—

The student commences with the first group; and after he has performed all the experiments given in the table of that group, several analyses are given him, each of which he examines for the members of this group. When he can perform these practical exercises correctly, he commences the second group—first performing the experiments in the group, and then analysing several solutions for the members of this group. When he can perform these correctly, he examines several solutions for the members of the first and second groups. In this progressive way he passes through the groups; so that by the time he has completed them he will have become an accurate analyst.

In the former Edition I proposed, and partially carried out, the division of the third group of bases, by employing ammonia as a group reagent; this alteration not only simplifies the subject, but it makes the plan of analysis taught in the laboratory more consonant with the methods adopted in actual practice. This alteration is fully carried out in this Edition, and a more complete description of the properties of the basic groups is given. I have also given in this Edition an outline of the special tests to be adopted in the detection of the acids, and considerable additions have been made in the Chapter on the Preliminary Examination of Solids. I have also introduced a new feature at the very commencement of the book; a series of experimental exercises are given, illustrating the principles upon which analytical operations are based, which it is intended the student should perform before he commences the groups. My aim in writing the book has been to furnish a suitable guide to the beginner; and I confidently hope that this Edition will be found superior to the former in this respect, and that it is what I wish it to be—a Student's Book.

R. G.

DUBLIN, *Nov.*, 1857.

CONTENTS.

PART I.

PAGE

PRELIMINARY REMARKS 1

HOW THE BOOK OUGHT TO BE STUDIED 3

SOURCES OF ERROR 6

ARRANGEMENTS OF THE RESULTS OF AN ANALYSIS . . . 7

FIRST BASIC GROUP.—Potassic, sodic, ammonic, and lithic oxides . 9

TABLE I.—Behaviour of the members of the group with the special reagents 10

Precautions to be attended to in the analysis of this group . . 12

Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of this group 13

General characters of the salts of this group . . . 17

Remarks on the individual members of the group, with additional special tests 18

Exercises on this group 24

SECOND BASIC GROUP. — Baric, strontic, calcic, and magnesic oxides 25

TABLE II.—Behaviour of the members of the first division of the second group with the special reagents 27

Precautions to be attended to in the analysis of this group . . 29

Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of this group 29

General characters of the salts of this group . . . 33

Remarks on the individual members of the group, with additional special tests 33

Exercises on this group 39

THIRD BASIC GROUP.—Zincic, manganous, nickelous, and cobaltous oxides 41

TABLE III.—Behaviour of the third group with the special reagents 42

Precautions to be attended to in the analysis of this group . . 44

PAGE
Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of this group 45
General characters of the salts of this group 49
Remarks on the individual members of the group, with additional special tests 50
Exercises on this group 56

FOURTH BASIC GROUP.—Aluminic, chromic, ferric, ferrous oxides; aluminic, chromic, and iron phosphates; the phosphates of the alkaline earths, baric, strontic and calcic oxalates; uranic and titanic oxides 58
TABLE IV.—Behaviour of the fourth group with the special reagents 60
Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of this group 61
General characters of the salts of this group 66
Remarks on the individual members of the group, with additional special tests 67
Exercises on this group 72
PROPERTIES OF THE PHOSPHATES AND OXALATES OF THE GROUP . 74
TABLE V.—Method for separating these phosphates and oxalates* . 78
Precautions to be attended to in their analysis 76
Other methods for the separation of these phosphates and oxalates, and other members of the group 77
Exercises on the phosphates and oxalates 81
Properties of uranic oxide 82
" of titanic oxide 83

FIFTH BASIC GROUP.—Auric, platinic, stannous, stannic, antimonious oxides; arsenious and arsenic anhydrides 84
METHODS FOR THE EXAMINATION OF THE GROUP 85
Properties of the metals, the oxides, the sulphides, the chlorides, and the hydrides, of As and Sb 88
General characters of the salts of this group 99
Remarks on the individual members, with their special tests . . 102
Exercises on this group 124

SIXTH BASIC GROUP.—Argentic, mercurous, mercuric, plumbic, bismuthous, cupric, and cadmic oxides 126
TABLE VI.—Behaviour of the sixth group with the special reagents . 128
Precautions to be attended to in the analysis of the group . . 131
Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of the group 132

PAGE
Remarks on the individual members of the group, with additional special tests 138
Exercises on this group 153
GENERAL PROPERTIES OF THE DIFFERENT BASIC GROUPS . . 156
TABLE VII.—Behaviour of the basic groups with the general reagents 160
Precautions to be observed in examining for the basic groups . 166
Exercises on the basic groups 170
CLASSIFICATION OF THE ACIDS 171
INORGANIC ACIDS 171
Behaviour of the inorganic acids and their radicals with reagents . 172
Chromic acid 172
Sulphuric acid 174
Sulphurous acid 175
Hyposulphurous acid 176
Boracic acid 176
Orthophosphoric acid 178
Pyrophosphoric acid 182
Metaphosphoric acid 182
Carbonic acid 183
Oxalic acid 185
Silicic acid 186
Hydrofluoric acid 189
Hydrosulphuric acid 191
Hydrochloric acid 193
Hydriodic acid 194
Iodic acid 197
Hydrobromic acid 197
Hydrocyanic acid 200
Nitric acid 203
Nitrous acid 207
Chloric acid 207
CLASSIFICATION OF THE INORGANIC ACIDS, INCLUDING OXALIC ACID . 209
GENERAL PROPERTIES OF THE INORGANIC ACIDS . . . 209
CHARACTERISTIC TESTS FOR THE INORGANIC ACIDS . . . 212
PREPARATION OF THE SUBSTANCES FOR THE EXAMINATION OF THE ACIDS, AND THE METHODS TO BE FOLLOWED IN THE EXAMINATION . 214
PRELIMINARY EXAMINATION FOR THE INORGANIC ACIDS . . 216
Exercises on the inorganic acids 217
ORGANIC ACIDS 219

PAGE
BEHAVIOUR OF THE ORGANIC ACIDS AND THEIR RADICALS WITH REAGENTS 219
Tartaric acid 219
Citric acid 222
Malic acid 224
Benzoic acid 225
Succinic acid 226
Tannic acid 227
Gallic acid 227
Acetic acid 228
Formic acid 229
Uric acid 231
CLASSIFICATION OF THE ORGANIC ACIDS 232
GENERAL PROPERTIES OF THE ORGANIC ACIDS 232
CHARACTERISTIC TESTS FOR THE ORGANIC ACIDS 234
PREPARATION OF THE SUBSTANCES FOR THE EXAMINATION OF THE ACIDS, AND THE METHODS TO BE FOLLOWED IN THE EXAMINATION 235
PRELIMINARY EXAMINATION FOR ORGANIC ACIDS 236
Exercises on the organic acids. 237
EXAMINATION OF LIQUIDS AND SOLIDS 238
PRELIMINARY EXAMINATION OF A LIQUID 238
Exercises 241
PRELIMINARY EXAMINATION OF SOLIDS 241
CLASSIFICATION OF SOLIDS 242
COLORATION OF THE GAS FLAME BY SOLIDS 243
TABLE VIII.—Examination of a solid in a glass tube closed at one end 248
Examination of a solid in an open tube 254
TABLE IX.—Examination of a solid on charcoal 257
TABLE X.—Examination of a solid with cobaltic nitrate, with sodic carbonate, and with borax 259
Fusibility of minerals 262
TABLE OF VOLATILE ELEMENTS WHICH CAN BE REDUCED AS FILMS . 266
SOLUTION OF A SOLID WHICH IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER 269
TREATMENT AND SOLUTION OF A SOLID WHICH IS NEITHER A PURE METAL NOR AN ALLOY, AND WHICH CONTAINS ORGANIC MATTER . 273
SOLUTION OF A PURE METAL OR AN ALLOY 276
Exercises 277

PART II.

ANALYSIS OF ORGANIC SUBSTANCES.

PAGE
PRELIMINARY REMARKS 279

ELEMENTARY ANALYSIS 280
Test of an organic compound 280
Tests for nitrogen 281
Tests for sulphur 282
„ phosphorus 282
„ inorganic substances 283

PROXIMATE ANALYSIS OF ORGANIC SUBSTANCES . . . 283
Analysis of the inorganic portion of organic substances . . 284
Animal chemistry 289

ALBUMINOID GROUP, ITS PROPERTIES 289
Properties and reactions of albumen 294
„ „ fibrin 299
„ „ casein 301
„ „ globulin 302
Recapitulation and remarks on the group 303

GELATIGENOUS GROUP, ITS PROPERTIES 304
Properties and reactions of gelatin 305
„ „ chondrin 307

SACCHARINE GROUP 309
Properties and reactions of milk sugar 309
„ „ glucose 309
„ „ inosite 312

ORGANIC BASES 313
Properties and reactions of urea 313
„ „ creatinine 316
„ „ creatin 317
ORGANIC ACIDS 317
Properties and reactions of lactic and sarcolactic acids . . 317
„ „ hippuric acid 318
„ „ glycocholic acid 319
„ „ glyco-hyocholic acid 320
„ „ taurocholalic acid 321
„ „ cystine 321
„ „ xanthine 322
„ „ cholestrin 323

PAGE
COLOURING MATTER 324
" " of the urine 324
" " " bile 324
" " " blood 324
Tests for blood 325
" bile 325

METHODS FOR ANALYSING QUALITATIVELY ANIMAL SECRETIONS . 326

QUALITATIVE ANALYSIS of urine 331
" " urinary calculi 335
PROPERTIES OF vegetable albumen 338
" " fibrine 338
" " caseine 339

THE SACCHARINE GROUP 339
Properties of cellulose 340
" starch 342
" gum 343
" cane-sugar 344
Exercises 346

ORGANIC BASES AND MECONIC ACID 347
Properties and reactions of nicotine 347
" " morphine 349
" " narcotine 352
" " quinine 354
" " cinchonine 356
" " strychnine 357
" " brucine 360
" " meconic acid 361

DETECTION OF OPIUM IN ORGANIC MIXTURES 362

METHODS FOR THE DETECTION OF THE POISONOUS ALKALOIDS IN ORGANIC MIXTURES 363
Exercises 367

PART III.

OPERATIONS 368
Solution 368
Precipitation 369
Filtration 371

PAGE
Decantation 371
Evaporation 372
Distillation 372
Ignition 373
Sublimation 373
Fusion 373
Deflagration 374
The blowpipe 374
Blowpipe lamps 376
Blowpipe supports 376
Blowpipe apparatus 377
Bunsen's gas lamp and the chief divisions of its flame . . 382
The six points in Bunsen's gas lamp flame 383
Method of examination in these different points of the flame . 384
Emission of light by substances 386
The melting-point of the flame 386
Flame-coloration 387
Oxidation and reduction of substances in the gas-flame . . 388
Reduction in glass tubes 388
Reduction on splinters of charcoal 388
Films upon porcelain 390
Examination of the films 391
Reactions of the elements in the gas-flame 393
Apparatus required in photo-chemical experiments . . . 394

REAGENTS 396
Hydrochloric acid 396
Nitric acid 397
Aqua regia 397
Sulphuric acid 398
Tartaric acid 399
Sodic hydric tartrate 399
Acetic acid 399
Hydrosulphuric acid 399
Sulphurous acid and anhydride 400
Chlorine-water 400
Hydrofluosilicic acid 400
Oxalic acid 401
Ammonic oxalate 401
Ammonia 401
Ammonic chloride 401
Ammonic sulphide 401
Ammonic carbonate 401

PAGE
Ammonic nitrate 401
Ammonic arseniate 402
Arsenic acid 402
Ammonic molybdate 402
Potassic sulphate 402
Potassic nitrite 402
Potassic ferrocyanide 402
Potassic ferricyanide 403
Ammonic sulphocyanide 403
Potassic sulphocyanide 403
Potassic chromate 404
Potassic cyanide 404
Sodic hydrate 404
Sodic carbonate 405
Disodic hydric phosphate 405
Sodic acetate 405
Sodic hydric sulphite 405
Borax 405
Sodic potassic carbonate 405
Sodic ammonic hydric phosphate 405
Dihydric dipotassic metantimoniate 406
Baric chloride 406
Baric nitrate 406
Lime water 407
Calcic chloride 407
Calcic sulphate 407
Magnesic sulphate 407
Baric carbonate 407
Ferrous sulphate 407
Ferric chloride 407
Plumbic acetate 407
Mercurous nitrate 407
Mercuric chloride 408
Cupric sulphate 408
Ammonio-sulphate of copper 408
Argentic nitrate 408
Ammonio nitrate of silver 408
Cobaltic nitrate 408
Platinic chloride 408
Auric chloride 409
Stannous chloride 409
Plumbic peroxide 409

PAGE
Copper turnings 409
Zinc 409
Nessler's test 409
Solution of indigo 410
Distilled water 410
Reagent papers 411
Preparation of blue litmus paper 411
" reddened litmus paper 411
" turmeric paper 411
Schonbein's test-papers for hydrocyanic acid 412
Preparation of Brazil wood paper 412

LIST OF APPARATUS REQUIRED FOR QUALITATIVE ANALYSIS . . 412

APPENDICES 413
Appendix A.—Treatment of silver residues 413
Appendix B.—Treatment of platinum residues 414
Appendix C.—Treatment of gold residues 415

PLATE OF APPARATUS REQUIRED FOR BUNSEN'S FLAME REACTIONS . 416

INDEX 417

QUALITATIVE ANALYSIS.

PART I.

PRELIMINARY REMARKS, 1. HOW THE BOOK OUGHT TO BE STUDIED, 6. SOURCES OF ERROR, 11. ARRANGEMENT OF THE RESULTS OF AN ANALYSIS, 12.

1. *Preliminary remarks.*—The object of *qualitative* analysis is to ascertain what elements are present, and how they are combined in substances of *unknown composition*. The object of *quantitative* analysis is to determine the quantity of each element present in substances. Hence, qualitative must always precede quantitative analysis, and in numerous cases it is not necessary to make a quantitative investigation, the *quality* of the substance affording all the information that is required. Qualitative and quantitative analysis, forming, therefore, two distinct branches of chemical analysis, are studied separately and independently of each other, and the study of the former, by which the component parts of substances are revealed, naturally precedes that of the latter.

2. The complete aim of qualitative analysis is to discover unknown as well as known bodies in substances, but it will be manifest that a course of qualitative analysis designed to teach students this branch of analytical chemistry must be more restricted; not only must the unknown form no part of the scheme, but those elements and compounds must also be excluded which, from their rarity or from their having no useful

application, are comparatively unimportant. Organic bodies, with the exception of a few of the more commonly occurring organic acids, are also excluded, and a student's course is confined, with the exception named, to the inorganic or mineral substances which are commonly met with in nature, or which have some useful application. A course of this kind is given in Part I of this book.

3. The methods of qualitative analysis consist in bringing the substance under examination in contact with *other bodies of known properties*, and observing the *phenomena* which ensue. These phenomena consist in alterations of *form* or *colour*, depending upon some *chemical change;* the change of form most frequent is the formation of a *precipitate* which, in many cases, possesses a characteristic colour, but sometimes *effervescence* takes place, and sometimes *deflagration*. The *bodies* with which the substance under examination is brought into contact are called *tests* or *reagents*, and the phenomena produced by their contact with the substance are called *reactions*. Acids, bases, salts, and elements are alike used as reagents, and the methods for preparing them in a state of purity, and the preparation of their solutions, are described in Part III of the book, along with a description of the principal operations employed in analysis, and a list of the apparatus required. Reagents employed for the detection of individual bodies are called *special reagents;* reagents which are employed to detect groups of substances are called *general* or *group reagents*. A special reagent is said to be *characteristic* when it produces a reaction so decisive that it admits of no mistake.

4. It has not only to be proved, in complete and accurate analytical investigations, that certain substances are present, but it has also to be proved, which is generally more difficult, that all other bodies but those discovered are absent. This cannot be accomplished by testing indiscriminately and separately for each base and acid radical; it requires, not only that the reagents be added in a certain order, but that the bodies which have to be sought for be separated *first into groups or families*, and afterwards each group divided and subdivided

until the presence or absence of each of its members is indubitably established. The separation of bodies into groups is effected by observing some chemical property common to several substances, and peculiar to them, by which means they can be classified into a group and all other bodies excluded.

5. The analyst by means of reagents interrogates the substance to be analysed as to what are its component parts; the reactions are the language in which the answer is returned. The student has, therefore, to learn the mode of questioning the substance and the language in which the answer will be conveyed; in other words, he has to learn, not only what general and special reagents are to be employed, but the order in which they are to be applied, and also the reactions they produce with the bases and acid-radicals, before he can attempt to search for these bodies in substances. No amount of *reading or lecture-hearing* will furnish the student with this knowledge; he can only obtain it by making the experiments himself of the different bases and acid-radicals with the reagents, and "*he must always reflect, before the addition of the reagent, for what purpose he applies it, and what are the phenomena he intends to produce,*" and the conditions indispensable for the production of correct and decisive reactions must be carefully observed, for a half knowledge in all deaprtments of science is of little worth, but in chemical analysis it is worse than useless. The phrase 'the behaviour or deportment of bodies with reagents' is frequently substituted for the term *reactions.*

6. *How the book ought to be studied.*—In the group tables the behaviour of the different members of the group with the special reagents are contrasted by placing them in parallel columns; the student has to perform these experiments, and to note the analogies and differences the members display with the same reagents. The order in which the experiments are to be made will be best explained by the aid of Table I; the experiments in the paragraphs marked A 1, B 1, and C 1, are first made, and in the order given; then those in A 2, B 2, and C 2; then those in A 3, B 3, and C 3; and, finally, those in A 4, B 4, and C 4. In making the experiments the con-

ditions which favour or prevent precipitation, together with the appearances of the precipitates, must be carefully noted and remembered, and in all the experiments the *chemical change* must be described, when possible, in the form of a diagram or equation in the student's note-book. The student, after he has made the experiments, will be able of himself to devise methods for the *separation* and *detection* of the different members; the knowledge he has acquired of the properties of the bodies places him, in fact, in the position of a judge who has to decide some cause, after having heard all the pleadings. He will also be able to decide whether more methods than one could be adopted for the separation of the members by the aid of the reagents given in the table. After he has devised a method for the separation of the members of a group, he compares it with the one given in the text. He may then proceed to perform the experiments on the different members given under the head of "Remarks on the Individual Members."

7. The student commences with the FIRST GROUP, and after he has performed all the experiments as previously described several solutions are given him, each of which he examines for the members of the group. When he can perform these practical exercises correctly, he proceeds to the SECOND GROUP, first performing the experiments and then analysing several solutions for the members. When he can perform these exercises correctly, he learns by experiment how to separate the twe groups by means of Table VII. He then analyses several solutions for the members of the first and second groups. When he has completed all the basic groups in the manner described, he should analyse about twenty different solutions, and look for all the bases given, after which the experiments given under the different acids must be performed. The student is then capable of undertaking a complete course of *qualitative analysis*, commencing with substances already in a state of solution, and concluding with the examination of solids.

8. In this edition the behaviour of the bases and acid radicals with a larger number of reagents has been given, and also more methods for the separation of substances. The student

ought, after he can analyse solutions for the members of a group by one method correctly, analyse other solutions of the same group by another method, and so learn all the different methods given for the separation and detection of the different members of any group. He ought, whilst studying each group, learn to prepare the solutions of the reagents in that group, and also the reagents themselves when methods for their preparation are given in Part III. He ought also to study carefully THE PROPERTIES OF THE METALS AND THE SALTS, and it would be well if he were to make some of the experiments there described; answers to the questions given on each group must also be written out.

9. The bases are divided into the following groups:

GROUP I.

Potassic Oxide.
Sodic Oxide.
Ammonic Oxide.

GROUP II.

1st Division.

Baric Oxide.
Strontic Oxide.
Calcic Oxide.

2nd Division.

Magnesic Oxide.

GROUP III.

Zincic Oxide.
Manganous Oxide.
Nickelous Oxide.
Cobaltous Oxide.

GROUP IV.

Aluminic Oxide.
Chromic Oxide.
Ferrous Oxide.
Ferric Oxide.

GROUP V.

Arsenious Acid.
Arsenic Acid.
Antimonous Oxide.
Stannous Oxide.
Stannic Oxide.
Auric Oxide.
Platinic Oxide.

GROUP VI.

1st Division.

Argentic Oxide.
Mercurous Oxide.
Plumbic Oxide.

2nd Division.

Plumbic Oxide.
Mercuric Oxide.
Bismuthous Oxide.
Cadmic Oxide.
Cupric Oxide.

10. We may here point out another advantage arising from the separation of substances into groups. It is as easy, for instance, to discover the absence or presence of a group as that of an individual substance; and the absence of a group being proved, it is unnecessary to examine further for any member contained in it.

11. *Sources of error.*—One frequent source of error with the young analyst is the imperfect mixture of the reagents with the solutions to which they are added. Another prolific source of error is the too liberal or the too sparing addition of the reagent, both being objectionable. To show the objectionable nature of a too sparing addition of the reagent, we will suppose the student to be examining a solution for barium and calcium; we will further suppose he has added potassic chromate and obtained a precipitate,* which proves the presence of Ba. He filters, and to the filtrate he adds ammonic oxalate to test for Ca; he obtains a precipitate with ammonic oxalate, although Ca is absent, because he has not added a sufficient quantity of the potassic chromate to precipitate all the Ba: thus, by the imperfect addition of a reagent, he arrives at a wrong conclusion. This fruitful source of error, viz., imperfect precipitation, may be avoided by adding to the filtrate a little more of the reagent with which the precipitation was effected. If this produces no further precipitate, the substance has been fully precipitated. Should a further precipitate be produced, it must be removed by filtration before attempting to throw down any other substance. The student must also carefully distinguish between the terms *precipitate* and *filtrate*, and be very particular in thoroughly washing the precipitates which require further examination. The wash-water must not be collected with the filtrate, if this last should be required for further examination. But all these precautions will have been

---

* Whenever a precipitate is obtained, it must be separated from the fluid by *filtration*, if either the fluid or the precipitate has to be examined further; the fluid for other substances, the precipitate for the detection of the several substances which may have been precipitated, or for the confirmation of any one substance.

attended to in vain should the experiments be performed in dirty apparatus, this being sufficient of itself to render the results unsatisfactory, if not erroneous.

12. *Arrangement of the results of the analysis.*—The student, during the course of his analytical studies, ought invariably to record the results of each analysis in his note-book, in a systematic and tabular form. An illustration is given to show the method to be pursued.

13. *Preliminary examination of a solid substance.*—1st. It is a colourless, crystallized substance, probably a salt. 2nd. Heated alone on charcoal, it deflagrates; a white, infusible substance remaining behind, which becomes luminous, and imparts a crimson colour to the flame, probably strontia. 3rd. Soluble in water; the solution is neutral to test-paper. As it is soluble in water, a large number of substances, all the insoluble salts, must be absent; as it is neutral to test-paper, all the salts of the alkalies and alkaline earths having an alkaline reaction must be absent; and the soluble salts of the other metals, with the exception of manganese and silver, must be absent, because their soluble neutral salts redden blue litmus paper.

14. The preliminary experiments indicate the presence of strontic nitrate.

15. *Examination for acids and acid radicals.*—The following acids, viz. CO_2, H_2S, As_2O_3, As_2O_5, and CrO_3, were proved to be absent on the examination for the bases.

16. The remainder of the acids, which give precipitates with a baric salt, could not be present; as they likewise form, with strontic salts, insoluble salts.

17. Added to a portion of the original solution $AgNO_3$, no precipitate; absent, Cl, Cy, Br, and I.

18. Added to another portion H_2SO_4, and copper turnings, nitrous fumes were evolved, showing the presence of nitric acid.

19. The examination for chloric acid yielded a negative result.

ACTUAL EXAMINATION.

On the addition of hydrochloric acid, no effervescence; absence of CO_2 and H_2S.

<table>
<tr>
<td rowspan="5">H Cl.
No precipitate.
Absent:
Ag_2O,
Hg_2O,
and probably
Pb O.</td>
<td rowspan="5">H_2S.
No precipitate.
Absent:
Hg O,
Pb O,
Bi_2O_3,
Cd O,
Cu O,
and
As_2O_3
As_2O_5
Sn O
SnO_2
Sb_2O_3
PtO_2
Au_2O_3</td>
<td rowspan="5">Boiled to expel H_2S; added a few drops of HNO_3; again boiled; added, lastly, NH_4Cl, and NH_4HO. No precipitate.
Absent:
Fe_2O_3, Al_2O_3, and Cr_2O_3
The substance being soluble in water, the phosphates and oxalates of the alkaline earths could not be present.</td>
<td rowspan="5">$(NH_4)_2S$.
No precipitate.
Absent:
Mn O
Zn O
Ni O
Co O</td>
<td colspan="2">$(NH_4)_2CO_3$.
A white precipitate formed.</td>
<td colspan="2">Divided the filtrate into two portions.</td>
</tr>
<tr>
<td colspan="2">May be present:
$BaCO_3$, $SrCO_3$, $CaCO_3$; dissolved in H$\bar{A}$; divided into two portions.</td>
<td>To one portion added, Na_2HPO_4</td>
<td rowspan="2">Evaporated the other portion to dryness, to expel ammoniacal salts. No residue.
Absent:
Na_2O, K_2O.</td>
</tr>
<tr>
<td>To one portion added $CaSO_4$</td>
<td>Precipitated the Sr from the other portion by H_2SO_4.</td>
<td rowspan="3">No precipitate.
Absent:
Mg O.</td>
</tr>
<tr>
<td rowspan="2">A precipitate, after lapse of sometime presence of Sr O, absence of Ba O.</td>
<td rowspan="2">Added to the filtered liquid NH_4HO, and H_2O.
No precipitate. Absent:
Ca $\overline{O}$.</td>
<td>Boiled a portion of the original solution with NaHO.</td>
</tr>
<tr>
<td>No ammonia evolved; absence of ammoniacal salts.</td>
</tr>
</table>

20. A few of the rarer elements and compounds have been given, but as they do not form a part of the course, they are not included in the tables; they are distinguished from the more commonly occurring ones by being printed in smaller type.

21. Part II is intended for advanced students.

PROPERTIES OF THE BASIC GROUPS.

First Group.

Potassic oxide (K_2O). Sodic Oxide (Na_2O). Ammonic Oxide ($(NH_4)_2O$). Lithic Oxide (Li_2O).

Solutions for the reactions.[*]—KCl, $NaCl$, NH_4Cl, $LiCl$, *in water.*

22. There are certain names in frequent use for these *oxides*, their *hydrates* and *salts*, which it is necessary for the student to be familiar with at the very outset. 1st. *Potash*, *soda*, *ammonia*, *lithia*, are names very frequently and indiscriminately employed for these oxides and their hydrates; but the terms *caustic potash*, *caustic soda*, &c., are strictly limited to the hydrates; thus the term caustic potash invariably signifies KHO. 2nd. These oxides, and *no others*,[†] are termed '*the alkalies*;' this term is also indiscriminately employed for the oxides and hydrates; but the term '*the caustic alkalies*' invariably signifies the hydrates. 3rd. Potash, soda, lithia, and their salts, are not volatile at a moderate heat, whilst ammonia and its salts are volatile; the first three are therefore frequently called the *fixed alkalies*, whilst the fourth is called the *volatile alkali*. 4th. Their salts are termed '*salts of the alkalies*,' or '*alkaline salts*;' and '*nitrates of the alkalies*,' '*alkaline*' *chlorides*,' and similar terms are in constant use.

---

[*] At the head of each group will be given the solution of salts which may be employed for the reactions.

[†] With the exception of two rare ones, viz. cæsic and rubidic oxides.

TABLE I.

BEHAVIOUR OF THE FIRST GROUP WITH THE SPECIAL REAGENTS.

$(NH_4)_2O$.	K_2O.	Na_2O.
A 1. Ammonia and its salts are *volatile*.	B 1. Potash and its salts are *not volatile*.	C 1. Soda and its salts are *not volatile*.
A 2. All ammonic salts are *decomposed* with the liberation of free ammonia, when any stronger base, such as CaH_2O_2,[*] KHO or NaHO, is added to their solutions. If the liquid be gently heated, the ammonia is volatilized, and its presence may then be recognised in three distinct ways. *α*. By its pungent *odour*. *β*. By turning *red* litmus paper *blue*. *γ*. By forming *white fumes*, when any volatile acid, as HCl, is brought into contact with it.[†]	B 2. When potassic salts are decomposed by a stronger base, KHO is liberated, but, *not being volatile* like ammonia, cannot be detected in a similar way.	C 2. When sodic salts are decomposed by a stronger base, NaHO is liberated, but, *not being volatile* like ammonia, cannot be detected in a similar manner.
A 3. $H_2C_4H_4O_6 = H_2\overline{T}$, in solution, produces in neutral or alkaline solutions of NH_4 a white crystalline precipitate of $NH_4HC_4H_4O_6 = NH_4H\overline{T}$, which is rather more soluble in water than the corresponding potassic salt. Vigorous shaking promotes the formation of this and the corresponding potassic salt.	B 3. $H_2\overline{T}$, in solution, throws down from neutral or alkaline solutions of K a white crystalline precipitate of $KH\overline{T}$. This salt, and the corresponding ammonic one, are soluble in free alkalies and free mineral acids. Slightly soluble in cold, much more so in hot water. (*Consult* par. 44.)	C 3. $H_2\overline{T}$ in solution, produces no precipitate in solutions of Na, except in *extremely* concentrated solutions, $NaH\overline{T}$ being soluble.
A 4. Ammonic compounds impart to a lamp flame *no* characteristic colour.	B 4. Potassic compounds tinge the outer lamp flame VIOLET. (*Consult* par. 46.)	C 4. Sodic compounds impart to the outer lamp flame an intense YELLOW colour. Small quantities of Na can by this means be detected in the presence of much K, the yellow flame overpowering the violet. (*See* par. 51.)

---

[*] If CaH_2O_2 is employed, it must be in the solid state, not in solution.

[†] This experiment is best performed by inserting a glass rod moistened with HCl into the mouth of the test-tube in which the decomposition of the ammonic salt is being effected, and immediately withdrawing it. The HCl employed should not be concentrated, but should be diluted with an equal volume of water. (*Consult* par. 40.)

23. **HOW TO ASCERTAIN THE PRESENCE OR ABSENCE OF EACH OF THE THREE MEMBERS OF THIS GROUP IN A SOLUTION WHICH CAN ONLY CONTAIN THESE THREE BASES.**—The only test for a potassic compound which can be relied upon in the presence of an ammonic one is the *flame reaction* (B 4), as the reagents which precipitate K from its solutions form precipitates similar in appearance with NH_4; it is necessary, therefore, to get rid of the ammonic compound, if one is present, before $H_2\overline{T}$ or $PtCl_4$ can be employed as a *characteristic* test for K; consequently ammonia has to be sought for first, and as the reagent employed for its detection would be an impediment (A 2) when searching for the other two members, we, on this account, test for ammonia in a *portion only* of the solution under examination; we divide, therefore, the solution into two parts, which we shall call A and B.

24. In A we examine for AMMONIA according to the method described in A 2 and par. 40, or by the one described in par. 42; these are characteristic tests for ammonia, distinguishing it from other substances. When ammonia is *absent* examine the B portion according to par. 25, and when it is *present* according to par. 26.

25. Examine for sodic and potassic compounds in the following way:—A clean (see Precautions, par. 28) platinum wire is dipped into the solution, and then introduced into the flame of a Bunsen's gas lamp. If the flame is coloured *yellow*, Na is present; if it is coloured *violet*, it proves the absence of Na (C 4) and the presence of K (B 4). *If* Na *is present*, examine for K by the photo-chemical method (par. 46). The *presence of* K may be *confirmed* by adding to the solution under examination, which must be cold (B 3), a solution of $H_2\overline{T}$ or $NaH\overline{T}$ (*see* par. 44) in excess, and shaking the mixed liquid very violently, and then allowing it to rest for some time; if a crystalline precipitate appears after this, K is present (B 3). The time required for the appearance of the precipitate depends upon the amount of K in the solution; if the quantity of K is small, the precipitate may not appear until several hours after the addition of the reagent.

26. The solution must be evaporated to dryness and ***ignited***, in order to volatilize the ammonic substance (A 1); the ignition must be continued as long as any white fumes or smoke are evolved. If a residue remains, after the expulsion of the ammonic body, one or both of the other two members of the group are present; this residue must be dissolved in the smallest possible quantity of water, and examined for K and Na, in the way described in the preceding paragraph.

27. WHEN THE EXAMINATION IS NOT CONFINED TO THE ALKALIES, BUT ALL, OR, AT LEAST, SOME OF THE OTHER BASES HAVE TO BE SOUGHT FOR IN THE SOLUTION, the solution, after being freed from all the other bases but MgO and those of the first group, must be evaporated to dryness, and ignited, to expel the ammonic salts, which have been added for their discovery. If a residue remain,[*] after the vapour of the ammonic salts has ceased to be evolved, it must be examined for K and Na, in the way described in par. 25. In this case—that is, when other bases besides those of the first group have to be sought for—NH_4 is to be tested for in a part of the *original solution.*

28. *The following precautions are to be attended to in the analysis of this group.*—Moist turmeric paper will turn *brown* by the mere exposure for a short time to the atmosphere of the laboratory, owing to the ammonia present in the air; this must be remembered in testing for ammonia in the manner described in par. 40. If the test-paper does not *brown* in the course of a *few seconds* or a *minute*, no ammonic compound is present, and the browning which may occur by longer exposure must be regarded as due to the ammonia in the air. In testing for potassic or sodic compounds by the lamp-flame, it is necessary that the platinum wire should be perfectly clean; this is secured by keeping it in the lamp-flame until it imparts no colour to it. Care should then be taken not to touch with the fingers that end of it on which the substance

---

[*] A fixed residue is not a certain proof of the presence of potash or soda, as it may arise from the presence of one of the non-volatile acids, viz. phosphoric, boracic, or silicic acid.

to be examined is to be placed. The flame reaction is not a reliable test for K in the presence of *organic matter*, as organic substances which burn with the separation of carbon colour the flame *violet;* organic matter, if present, must be got rid of by *igniting* the substance if it is a solid, or if a solution by evaporating it to dryness, and then igniting the residue; in either case the solid after ignition ought to be dissolved in a small quantity of water and filtered, if, after the water is added, any brownish-black particles appear. Young students seldom continue the ignition for the expulsion of the ammonic salts sufficiently long, and if these solids are not completely expelled precipitates will be obtained with $H_2\bar{T}$, $NaH\bar{T}$. $PtCl_4$, which will be regarded as indicative of the presence of a potassic compound. The solution must be as concentrated as possible for the detection of K by $H_2\bar{T}$ or $NaH\bar{T}$, and the student is directed to par. 44 as regards the neutrality, acidity, and alkalinity of the liquids.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, THE SULPHATES, OF THIS GROUP.

29. *The metals.*—K, Na, and Li are lighter than H_2O. Li is the lightest of all known solids; the sp. gr. of Na is 0·985, that of K is 0·865, and that of Li 0·589. K melts at 62·5° C., Na at 95·5° C., and Li at 180° C. At a red heat K and Na may be distilled; the vapour of K is a beautiful green colour, that of Na is colourless; Li is volatile at high temperatures. These three metals oxidize on exposure to air; K is the most and Li the least oxidizable of the three; they decompose water at all temperatures, uniting with the oxygen and liberating the hydrogen; K decomposes it most rapidly, the hydrogen taking fire from the heat evolved by the combination of the metal with O. They combine directly with Cl, I, Br, S, &c.

30. *The oxides.*—K_2O, Na_2O, Li_2O may be obtained either by introducing the metals into an atmosphere of oxygen or by heating the metals and their hydric oxides together in equiva-

lent proportions. K_2O and Na_2O melt at a red heat, and volatilize without decomposition at very high temperatures; these two oxides attract H_2O very rapidly from the air, and after they have become hydrated they cannot be dehydrated by heat alone. These anhydrous oxides are instantly converted into the hydrates on being brought into contact with H_2O, and it is in the form of hydrates they are employed in the laboratory and in the arts; the anhydrous oxides are, therefore, unimportant.

The hydrates.—KHO and NaHO are usually prepared from K_2CO_3 and Na_2CO_3, by adding to boiling solutions of these salts CaH_2O_2 until the clear solution no longer effervesces on the addition of HCl in excess. They may also be obtained, and it is in this way that LiHO is generally prepared, by adding to a solution of their sulphates a solution of BaH_2O_2. These hydrates are white solids; they melt below redness, and KHO and NaHO volatilize at a pale red heat; LiHO does not appear to volatilize at a white heat. KHO and NaHO absorb H_2O and CO_2 from the air; by the absorption of the H_2O they are converted into syrupy liquids; as they become transformed into carbonates, the syrupy solution of the potash continues, whereas the soda becomes converted into an efflorescent paste, because K_2CO_3 is deliquescent and Na_2CO_3 is not; LiHO absorbs CO_2 from the air, but not H_2O. They are soluble in water and alcohol; LiHO is the least soluble of the three. Their aqueous solutions are very alkaline and absorb CO_2 from the air. These alkalies are not reducible by H; KHO and NaHO are reducible by C, the K and Na passing off in vapour; but Li and the metals of the next group, although they have less affinity for O than K and Na, cannot be obtained in this manner, their oxides not being reducible by C because the metals are not sufficiently volatile to pass off in vapour. Heated in a current of Cl, they are converted into chlorides with disengagement of O. A current of Cl passed into their *solutions* converts them into a mixture of alkaline chlorides, and, according to the strength of the solution and the temperature, *alkaline hypochlorites* or *chlorates;*

if the solutions are weak and not heated, hypochlorites are produced, when these conditions are reversed the chlorates are formed. When fused with S at a temperature not above 200° C., or if the S is boiled in their solutions, an alkaline hyposulphite and an alkaline polysulphide are formed; but if the reaction takes place at a red heat an alkaline sulphate and an alkaline pentasulphide are produced. By the action of P on the alkalies a mixture of alkaline hypophosphites and phosphides is formed. The alkalies dissolve alumina and silica, and attack glass and porcelain; the student will study the behaviour of the insoluble basic oxides with the alkalies in the next groups.

31. NH_4.—This radical has never been obtained uncombined; when set free from its combinations it decomposes at the same moment, if it exists at all, into NH_3 and H. Although it has never been isolated, the theory of its existence is considered to derive great support from the fact that Hg forms with NH_4, as it does with the true metals, an *amalgam*. This compound of Hg and NH_4 is easily obtained by introducing sodium amalgam into a strong solution of NH_4Cl; the Na rapidly dissolves by combining with the Cl, the liberated NH_4 combining with the Hg; a soft buttery mass is thus obtained, occupying an enormous volume compared with that of the Hg by itself.

32. NH_3 and NH_4HO.—The name *ammonia* has been given to these two different compounds; the first is a gas, and the other is obtained by dissolving the gas in water; the same name was given to the gas and its solution, because it was considered the gas suffered no chemical change by its solution in water, inasmuch as it (NH_3) is not only expelled from the solution by heat, but it even escapes from it at the ordinary temperature of the air; and the solution likewise retains the *smell* and other properties of the gas; hence the gas and its solution was regarded as the same *chemical* compound. They are now viewed as two distinct compounds. It is supposed that when NH_3 is dissolved in H_2O, they enter into combination in equivalent proportions, NH_4HO (ammonic

hydrate) being formed, corresponding to KHO and NaHO, the compound radical NH_4 having functions similar to the simple bodies K and Na. The radical NH_4 is supposed to exist in all ammonic salts, whether the salts be formed by the action of the acids on NH_4HO or on NH_3; thus—

$$(1)\ 2NH_4HO + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O.$$

$$(2)\ 2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

NH_3 is remarkable for its pungent and peculiar smell, which is shared by the hydrate; the gas and the liquid have a strong alkaline reaction, and they both neutralize the strongest acids.

33. *The sulphides*, including the ammonic, may be obtained by dividing a solution of them into equal portions, and passing through one portion H_2S to saturation; an alkaline sulph-hydrate (MHS) is formed; on adding to this the other portion, the sulphide is produced; thus, $MHS + MHO = M_2S + H_2O$; K_2S and Na_2S may be obtained by deoxidizing their sulphates with H or C at a red heat. Their solutions have an alkaline reaction, and are colourless at first, but after a time they become coloured from absorbing O from the air, and becoming transformed into a mixture of free alkali and a polysulphide. If heated in contact with the air or O, they become converted into sulphates. They readily dissolve S, and are converted into polysulphides. Acids decompose them with liberation of H_2S.

34. The *chlorides* may be formed by dissolving the alkalies or their carbonates in HCl; these salts are soluble in water, and are sparingly soluble in spirit of wine; their solutions are neutral to test paper. NH_4Cl does not volatilize at 100° C., but at higher temperatures it volatilizes readily without decomposition; heated in open vessels, KCl, NaCl, and Li Cl volatilize at a red heat. The double salts they form with $PtCl_4$ are noticed in pars. 41, 45, 55, 57. KCl and NaCl, when evaporated with excess of $H_2\bar{O}$ and HNO_3, are converted into oxalates and nitrates, and on igniting these two chlorides

with $(NH_4)_2\bar{O}$, alkaline carbonates are formed in considerable quantities.

35. The *nitrates* may be formed by adding HNO_3 to the alkalies or their carbonates. They are readily soluble in H_2O, only slightly soluble in spirit of wine; their solutions are neutral to test-paper. They liquefy on application of heat; at a red heat $NaNO_3$ and KNO_3 are converted by the expulsion of one third of their O into nitrites, and at a still stronger heat a further quantity of O, along with all the N, is expelled, and a mixture of the pro- and per-oxides of the metals remains; at 108° C., NH_4NO_3 liquefies, and at 249° C. it undergoes complete decomposition into N_2O and H_2O. The fixed alkaline nitrates heated with C and with S are converted into carbonates and sulphates, the N being expelled; when they are ignited with NH_4Cl, or in a current of dry HCl gas, they are converted into chlorides; and if *repeatedly* evaporated with excess of liquid HCl, they are completely converted into chlorides. If they are also repeatedly evaporated with $H_2\bar{O}$ in excess, they are converted into oxalates.

36. *The sulphates* may be formed by adding H_2SO_4 to the alkalies or their carbonates, or by evaporating the nitrates or chlorides with H_2SO_4. They are soluble in water; the solution of those the general formula for which is M_2SO_4 is neutral to test-paper; the solution of those whose general formula is $MHSO_4$ is acid to test-paper. K_2SO_4 and Na_2SO_4, at a white heat, are slightly decomposed; $(NH_4)_2SO_4$ melts at 140° C., and between 260° C., and 315° C. it volatilizes and undergoes decomposition, $(NH_4)_2SO_3$ being among the products. Fe decomposes K_2SO_4 and Na_2SO_4 at a red heat, the alkalies are liberated, and a mixture of sulphide and oxide of iron formed; they are converted into chlorides by ignition with NH_4Cl, and we have already noticed (33) they are deoxidized by ignition with C. One of the two atoms of radical in these sulphates can be replaced by one of the other radicals, or by H; thus, NH_4NaSO_4, $KHSO_4$, &c.

37. *General characters of the salts of this group.*—The metals of this group, compared with those of the other groups,

furnish the largest number of salts soluble in water; the sodic salts are almost all soluble in H_2O, hence there are no very good direct tests for sodic compounds, and owing to the greater number of the salts of these metals being soluble, we have no group or general reagents for this group as we have for the other groups. Not only are the oxides soluble in H_2O, but also their sulphides, sulphates, oxalates, carbonates, phosphates, nitrates, and other salts. The sparing solubility of lithic phosphate and carbonate in H_2O distinguishes it from the other members of the group, and renders it more nearly allied in this respect to the next group. The solutions of the sulphides and carbonates, as well as the solution of the alkalies themselves, restore the blue colour to reddened litmus, and impart an intensely brown tint to turmeric paper. The salts of these bases are colourless, provided the constituent acid be so.

REMARKS ON THE INDIVIDUAL MEMBERS OF THE GROUP, WITH ADDITIONAL SPECIAL TESTS.

38. NH_4 *and its compounds.*—NH_3, we have already stated, is remarkable for its pungent smell, and it exerts a powerfully corrosive action on moist animal tissues, hence serious consequences might arise from inhaling a considerable quantity. The white fumes produced when NH_3 is brought into contact with a volatile acid are due to the formation of a solid ammonic salt. All ammonic salts containing volatile acids, on being heated, volatilize either with or without decomposition; but the ammonic salts of the non-volatile acids, viz. phosphoric, boracic, and silicic, are decomposed by heat; the ammonia escapes, but the non-volatile acid remains behind.

39. When organic substances containing N decay and putrefy, ammonic carbonate is constantly produced; the same salt is likewise formed when nitrogenized organic substances are submitted to destructive distillation.

40. The following modification of the test (A 2) for ammonia is to be preferred—If the *substance* is in solution, mix it in a small beaker, with sufficient CaH_2O_2 to render the

mixture solid; but if it is a *solid*, moisten it slightly with H_2O before mixing it in the beaker with excess of CaH_2O_2 The beaker is covered, after the mixing, with a glass plate, on the lower side of which adheres a small piece of moist turmeric or moist reddened litmus paper.

41. $PtCl_4$ produces in neutral and acid ammonic, as in potassic, solutions, a yellow crystalline precipitate, $2NH_4Cl, PtCl_4$, very sparingly soluble in alcohol.

42. If a solution of HgK_2I_4 in KHO be added in excess to a liquid containing a trace of NH_4HO or its salts, it assumes a brownish tinge or furnishes a brown precipitate, according as the proportion of the ammonic compound is less or more, tetramercuric diammonic diniodide being formed, thus:—

$$4HgK_2I_4 + 6KHO + 2NH_4HO = Hg_4N_2I_2, 2H_2O + 14KI + 6H_2O.$$

This test is called Nessler's test.

Characteristic.—The reactions with CaH_2O_2 (40), and with Nessler's test.

43. K *and its compounds.*—K is of a bluish-white colour; it is brittle at 0° C.; a little above this temperature it is malleable; at 16° it is soft; at 62·5° it is liquid, and at a red heat it may be distilled; when freshly cut, it possesses considerable lustre, but instantly oxidizes on exposure to the air; it can only be preserved in the metallic state by keeping it in some liquid, like coal naphtha, which contains no oxygen, or in exhausted hermetically sealed glass tubes. It occurs in felspar, mica, &c., as silicate, in combination with aluminic and other silicates. It is also found as sulphate, nitrate (saltpetre), and in a mineral called carnallite, which is a double hydrated potassic and magnesic chloride ($KCl, MgCl_2, 6H_2O$), which occurs above the bed of rock salt at Stassfurth, near Magdeburg.

44. $NaH\overline{T}$* is a much more delicate test for K than $H_2\overline{T}$, because $KH\overline{T}$ in neutral solutions is soluble in acids, and an acid must be set free whenever $H_2\overline{T}$ is added to a solution containing a potassic salt. If the solution is acid, the free acid

---

* My friend, Mr. W. Plunkett, suggested the employment of $NaH\overline{T}$. *See* 'Chemical Gazette,' vol. xvi, p. 217.

must be expelled, if practicable, by evaporation or ignition; or if not expelled, it must be neutralized with $NaHO$ or Na_2CO_3 before testing for K either with $NaH\overline{T}$ or $H_2\overline{T}$. $NaH\overline{T}$ cannot, of course, replace $H_2\overline{T}$ as a test for K when the solution to be tested contains a free alkali, because $KH\overline{T}$ is soluble in free alkalies; but when the bases of the other groups are sought for, the solution cannot be alkaline when we arrive at the examination for K, and it is not often that we have to deal with an alkaline solution, even when the alkalies are the only bases that have to be examined for.

45. $PtCl_4$ produces, in neutral and acid solutions of K, a yellow crystalline precipitate[*] of $2KCl, PtCl_4$. The presence of HCl promotes the formation of this precipitate. It is slightly soluble in water, but wholly insoluble in alcohol. This is a very delicate test for any potassic compound; the best method of applying it is to mix the solution with $PtCl_4$, evaporate to dryness upon a water-bath, and treat the residue with alcohol; the excess of $PtCl_4$ dissolves in the alcohol, colouring the solution yellow; $2KCl, PtCl_4$ is left undissolved as a yellow crystalline precipitate. The addition of $PtCl_4$ should always be preceded by that of HCl, to convert the potassic compound into the chloride, if it should not exist already in that form.

46. If a small particle of a potassic compound be introduced on the loop of a platinum wire into the flame of a *Bunsen's gas-lamp*, it will, if volatile at the temperature of the flame, *colour* the part of the flame above the sample *blue-violet;* if the substance examined contains a sodic as well as a potassic compound, the yellow colour imparted to the flame by the sodic compound overpowers and obscures the violet tint produced by the potassic one. But K can be detected in the

---

[*] $PtCl_4$ gives with iodine a dark red colour; and as this colour prevents the yellow precipitate of $2KCl, PtCl_4$ from being distinctly seen, iodine should be expelled, if present, before testing for K by this reagent. To expel it, evaporate to dryness with *concentrated* HNO_3; dissolve the residue in water, and add HCl and $PtCl_4$, and then proceed in the usual way.

presence of Na (or Li) if we look at the flame through deep blue cobalt glass;* through this coloured glass no coloured rays from Na (or Li) can pass, but it transmits those peculiar to K. The flame, when viewed through this coloured glass, is of an intense violet colour, and is even visible when one part of potash is present with two hundred parts of soda. As all substances which make flame luminous, especially all organic substances which burn with separation of carbon, give the same violet colour, these substances must first be removed by heat before the colour of the flame can be used as a test for K.

47. The potassic flame may be viewed through the indigo prism instead of the blue glass; the flame appears through the prism of *sky blue*, then *violet*, and at last of an intense *crimson red*, even when seen through the thickest layers of solution; admixtures of Na or Ca do not hinder the reaction.

48. The potassic flame viewed through the violet coloured glass appears violet, and through the green coloured glass blue-green.

49. The more volatile the salt, the more intense is the coloration it imparts to the flame; potassic chloride and potassic nitrate volatilize rapidly, the carbonate and sulphate less rapidly, and the phosphate still more slowly, but they all of them distinctly show the reaction, though decreasing in degree. The sensibility of the test may, in many cases, be increased by moistening the substance under examination with H_2SO_4, drying the substance at the border of the flame, and then introducing it into the melting space. With silicates and other difficultly volatile potassic compounds the reaction is best secured by fluxing it with pure gypsum in the melting space; there is formed a calcic silicate and volatile potassic sulphate which colours the flame. It is advisable to ignite decrepitating salts in a platinum spoon before attaching them to the loop of the platinum wire.

---

* The cobalt blue glass can be obtained at the operative chemists. Before using the glass, it must first, of course, be ascertained how small a quantity of potash mixed with soda (or lithia) it will clearly indicate.

Characteristic.—The flame test, the reaction with $PtCl_4$ and $NaH\bar{T}$.

50. Na *and its compounds.*—The colour of this metal is bluish-white; in properties it much resembles K. The salts of this base, with a few exceptions, are very soluble; the means we have of detecting it are therefore limited. It exists in the mineral kingdom as CHLORIDE (*kitchen salt*), SULPHATE (*Glauber's salt*), BORATE (*borax or tincal*), NITRATE and CARBONATE. It likewise forms a constituent of many SILICEOUS MINERALS.

51. If a small particle of a sodic compound be introduced, on the loop of a platinum wire, into the melting space of the flame of a *Bunsen's gas lamp*, it will, if volatile at the temperature of the flame, colour the part of the flame above the sample intense yellow; this is the most characteristic test for sodic compounds. If the sodic flame is made to illuminate a crystal of potassic bichromate, this salt appears perfectly colourless and transparent, and with an adamantine lustre. The following reaction is even more delicate. A piece of paper about a centimètre square is coated with red mercuric iodide, and placed upon a small holder, which is movable on an arm, also movable, attached to the chimney of the lamp. When the least quantity of NaHO, Na_2SO_4, or NaCl, is introduced into the melting space of the flame, the red iodide becomes white, with a faint tinge of fawn colour. The glaring contrast of these colours is apparent when the paper is lit up by being placed close to the red-hot wire and bead, and the wire then placed in the flame, that the bead only reaches the melting space. Potassic, lithic, and calcic compounds do not interfere with this reaction.

52. The sodic flame appears *orange*-yellow, through the green glass, even with the smallest quantities. This glass is particularly adapted to the recognition of all sodic compounds (Merz).

53. Although the sodic salts are a little less volatile than the potassic salts, they display, with regard to their relative volatility, and the influence of H_2SO_4 and pure gypsum in in-

creasing their sensibility, the same behaviour as the potassic ones.

54. Di-hydric di-potassic metantimoniate ($K_2H_2Sb_2O_7$) produces, in neutral or alkaline solutions of sodic salts, a white crystalline precipitate of $Na_2H_2Sb_2O_7$. In concentrated solutions the precipitate is formed immediately; but from dilute solutions it separates only after the lapse of some time. Violent agitation of the fluid promotes the separation of the precipitate. Acid solutions decompose the potassic salt, antimonic acid being precipitated; free acids must therefore be first neutralized with potash before this test can be applied. $Na_2H_2Sb_2O_7$ is soluble in K_2CO_3; if this substance be present in the solution it must be nearly saturated with acetic acid.

55. The double chloride of 2NaCl, $PtCl_4$ is soluble in alcohol, and very soluble in water; therefore $PtCl_4$ produces no insoluble salt with sodic compounds, either in an aqueous or alcoholic solution.

Characteristic.—The flame reaction.

56. Li *and its compounds.*—Lithia occurs in certain minerals, particularly in spodumene, petalite, and lepidolite.

57. Na_2HPO_4 produces in not over dilute solutions of lithic salts, upon boiling, a heavy white crystalline precipitate of Li_3PO_4; if the solution is then evaporated to dryness, and the residue treated with cold water, the lithic phosphate remains undissolved. We can, therefore, in this way distinguish Li from, and in the presence of, K and Na. LiCl forms with $PtCl_4$ a double salt, 2LiCl, $PtCl_4$, which is even more soluble in water than the corresponding sodic salt, 2NaCl, $PtCl_4$.

58. "If a lithic salt, particularly LiCl, is exposed on a platinum wire in the melting space of the flame of a Bunsen's gas-lamp, the outer flame shows a strong CARMINE tint. Presence of sodic salts, but not potassic salts, conceals this reaction."

59. If the lithic flame be viewed through the indigo prism, it appears through the thinnest layer of the indigo solution of a *carmine-red*, which, with increasing thickness of the solution, becomes *gradually feebler*, and *disappears* before the thickest layers pass before the eye; whereas the potassic flame appears through the thinnest layer of the indigo solution of a *sky-blue*, then *violet*, and at last of an intense *crimson-red*, even when seen through the thickest layers of the solution. Admixtures of sodic or calcic compounds do not hinder the reaction of either the Li or K.

60. As of all lithic compounds the carbonate and chloride give the most intensely coloured flame, it is only necessary to mark on the prism the place at which the lithic rays from these salts disappear, to obtain a space above this mark which transmits only red potassic rays. As this part of the prism acts in the same way as a thick cobalt glass in detecting potassic compounds in the presence of sodic ones, the cobalt glass can be dispensed with for detecting K.

61. Lithia with an admixture of potash is detected by bringing a sample into the melting space, and comparing its flame with that of a sample of pure potash placed side by side with it in the melting space. With thin layers of the solution the lithic flame appears redder than the pure potassic flame; with somewhat thicker layers the flames are equally red, if the proportion of lithia to potash be very small; if the lithia be in excess, the intensity of the red lithic flame sensibly diminishes with thicker layers, while the red flame of potash is scarcely weakened. In this manner a few thousandths of lithia may be detected in the presence of potash. Soda has almost no influence on the reaction.

62. *Characteristic.* The flame test and the reaction with Na_2HPO_4.

63. Answers to the following exercises must be written out.

EXERCISES.

1. In what state are K and Na found in nature?

2. Describe the different parts of a flame, and explain the action of those in blow-pipe experiments.

3. Describe a method for the preparation of sodic hydric tartrate.

4. Knowing that N_2O is produced by subjecting dry NH_4NO_3 to heat, what gas would you infer would be produced by subjecting NH_4NO_2 to heat?

5. Under what circumstances would you employ tartaric acid in preference to sodic hydric tartrate as a test for K?

6. Describe some of the physical and chemical properties of K and Na.

7. Account for the formation of ammonic sulphide and carbonate in the manufacture of gas from coal.

8. State how you would prepare $PtCl_4$.

9. Describe the preparation and application of the test called "Nessler's test."

10. Do solid KHO and NaHO undergo any change on exposure to air; and if so, name the changes and any differences which they may exhibit.

11. What are the characteristic tests for K, Na, and NH_4?

12. How are the alkaline hydrates prepared?

13. Describe as many methods as you are able for distinguishing K from Na.

14. Describe a method for the preparation of $K_2H_2Sb_2O_7$.

15. Show by means of an equation the chemical changes which take place in the preparation of $KClO_3$ from the action of Cl on KHO.

16. Show by means of equations the action of sulphur on the fixed alkalies at different temperatures, and the action of phosphorus on the fixed alkalies.

17. To what are the terms 'precipitation,' and 'evaporation,' and distillation applied?

18. What is the difference between a simple and a chemical solution?

SECOND GROUP.

Baric Oxide (BaO), Strontic Oxide (SrO), Calcic Oxide (CaO), Magnesic Oxide (MgO).

Solutions for the reactions.—$BaCl_2$, $SrCl_2$, $CaCl_2$, $MgSO_4$, in water.

64. 'Baryta,' 'Strontia,' 'Lime,' 'Magnesia,' are names very frequently given to these oxides, they are also employed occasionally to signify the hydrates of the oxides; but if the term *caustic* be employed along with them, they refer then exclusively to the anhydrous oxides. These oxides and their hydrates are called "the alkaline earths," and their salts are called "the salts of the alkaline earths."

65. $(NH_4)_2CO_3$ precipitates Ba, Sr, and Ca completely from

their solutions as carbonates, but it precipitates Mg *only partially*, and this partial precipitation is prevented, at least for a time, if NH_4Cl is present in the solution (see par. 108). Owing to this difference in their behaviour with $(NH_4)_2CO_3$, the group is subdivided; the members of the first division are BaO, SrO, and CaO; MgO forms the second. The *group reagent* for the first division is $(NH_4)_2CO_3$, its addition is *preceded* by that of NH_4Cl and NH_4HO. The *reagent* for MgO is Na_2HPO_4, but as it also precipitates the members of the first division, it can only be employed for MgO after the removal, or in the absence, of BaO, SrO, and CaO.

66. *Examination for the members of the first division.*—When a solution is examined for the members of this division *only*, the group reagent must be added, and as directed at par. 369.

67. The precipitate produced by the group reagent, after being well washed, must be dissolved in *acetic acid*, and the solution divided into two parts, which we shall call A and B.

68. *Add a solution of (not too little)* $CaSO_4$, *to the* A *portion.*—As $CaSO_4$ precipitates Ba *immediately*, Sr *after the lapse of some time*, and Ca *not at all* (*see* D 1, E 1, and F 1), one of three cases will occur on the addition of $CaSO_4$ to the A portion; either there will be *no precipitate*, or there will be *one after the lapse of some time*, or there will be an *immediate one*. If there is no precipitate, examine according to par. 69; if there is one after the lapse of some time, examine according to par. 70; if there is one immediately, examine according to par. 71.

69. As Ba and Sr are absent, add to the B portion NH_4HO and a solution of $(NH_4)_2C_2O_4$; if a precipitate is produced, Ca is present.

TABLE II.

BEHAVIOUR OF THE MEMBERS OF THE FIRST DIVISION OF THE SECOND GROUP WITH THE SPECIAL REAGENTS.

BaO.	SrO.	CaO.
D 1. $CaSO_4$, in solution, prepitates Ba *immediately*, from its solutions, as $BaSO_4$, which is insoluble in acids and alkalies.	E 1. $CaSO_4$, in solution, precipitates Sr *after* the *lapse of some time*,* from its solutions, as $SrSO_4$, which is almost absolutely insoluble in acids and alkalies.	F 1. $CaSO_4$ produces *no* precipitate in solutions of Ca.
D 2. K_2CrO_4, in solution, produces, in neutral and alkaline solutions of Ba, a pale yellow precipitate of $BaCrO_4$, insoluble in the alkalies and acetic acid, soluble in HCl and HNO_3.	E 2. K_2CrO_4, in solution, produces in *concentrated*, but not in *dilute*, solutions of Sr, or such as contain *free acetic acid*, a bright yellow precipitate of $SrCrO_4$.	F 2. K_2CrO_4, in solution, produces no precipitate in solutions of Ca, $CaCrO_4$ being soluble.
D 3. H_2SO_4 and *the soluble sulphates* behave in the same manner in solutions of Ba as $CaSO_4$.	E 3. H_2SO_4 and the *soluble sulphates* precipitate Sr from its solutions, as $SrSO_4$. The precipitate will not appear immediately, unless the solution be very concentrated.	F 3. H_2SO_4 and the *alkaline sulphates* cause only in concentrated solutions of Ca a partial precipitate of $CaSO_4$, which redissolves completely in a large amount of water.
D 4. $H_2C_2O_4$, in solution, produces only in concentrated solutions of Ba a white precipitate of BaC_2O_4, soluble in acids. The addition of NH_4HO renders this reaction therefore more susceptible.	E 4. $H_2C_2O_4$, in solution, precipitates, even from dilute solutions of Sr, a white precipitate of SrC_2O_4. The addition of NH_4HO promotes the formation of the precipitate.	F 4. $H_2C_2O_4$, in solution, throws down from neutral solutions of Ca, even if highly diluted, a precipitate of CaC_2O_4. The addition of NH_4HO renders this reaction more delicate.

* The formation of the precipitate is much promoted by agitation.

70. Ba is *absent*, Sr *is*, and Ca *may be*, *present*. The presence or absence of Ca cannot be determined, as long as any Sr remains in solution; because the reagents, which precipitate Ca, precipitate Sr also (E 3, F 3, E 4, F 4). We add, therefore, to the B portion *dilute* H_2SO_4, which precipitates all the Sr (E 3), and only a small portion of Ca in a concentrated and none at all from a dilute solution (F 3); in any case, sufficient Ca remains in solution for detection. Filter off from the precipitate produced by the H_2SO_4, after sufficient time (one or two hours) has been allowed for the precipitation of the $SrSO_4$, and add to the filtrate NH_4HO in excess, and then $(NH_4)_2C_2O_4$, which will cause a precipitate if Ca is present.

71. Ba *is*, and Sr and Ca *may be*, *present*. As $CaSO_4$ cannot be employed to detect Sr in the presence of Ba, and as Ba causes a precipitate with all the reagents which precipitate Sr and Ca, the former must be got rid of before we can ascertain the absence or presence of the two latter substances. For this purpose, K_2CrO_4 must be added to the B portion, which precipitates Ba only (D 2, E 2, F 2); filter, and to the filtrate* (which will be of a yellow colour, from the excess of K_2CrO_4, if the Ba has been completely precipitated) add NH_4HO in excess and $(NH_4)_2CO_3$, and warm the solution; if a *precipitate is produced*, it may be due to the presence both of Sr and Ca; if *no precipitate is produced*, Sr and Ca *are absent*. If a precipitate is produced, wash it until all excess of K_2CrO_4 has been removed, then dissolve it in acetic acid, filter, if necessary, through a very small filter, and add to the clear solution not too small a quantity of the dilute solution of K_2SO_4,† after which addition the solution must be well agitated; if the

---

* It is absolutely necessary to have the filtrate from the $BaCrO_4$ perfectly bright and transparent, which sometimes is troublesome to obtain. See filtration in Part III.

† Care must be taken to make the solution of K_2SO_4 of the strength directed in the list of reagents. Of that strength, it contains the same quantity of SO_4 as a saturated solution of $CaSO_4$ contains in a like quantity of liquid; it is, therefore, sufficiently strong to precipitate SrO, but not to precipitate CaO.

K_2SO_4 produces a precipitate, after the lapse of some time, Sr is *present*. If the K_2SO_4 solution has produced a precipitate, add some dilute H_2SO_4 to complete the precipitation, and allow sufficient time (one or two hours) for the complete separation of the $SrSO_4$ before filtering; add to the filtrate, or to the solution, without filtering, if K_2SO_4 has produced no precipitate, NH_4HO *in excess* and $(NH_4)_2C_2O_4$; if this last reagent produces a precipitate, Ca is present.*

72. The filtrate from the $(NH_4)_2CO_3$ or the solution with which $(NH_4)_2CO_3$ has failed to give a precipitate, must be examined for Mg as directed at par. 372.

73. *The following precautions are to be attended to in the analysis of this group.*—The solution of $CaSO_4$ must be added in not too small a quantity, and it must always be added in the cold, as this reagent is less soluble in hot than cold water. Time must be allowed for the formation of the precipitate produced by this reagent in solutions of Sr, the formation of which is much promoted by agitation. In separating Sr from a solution by K_2SO_4, the liquid ought not to be filtered immediately, but a due time allowed for the complete separation of the precipitate from the solution; and the solution ought not to be warmed, owing to the less solubility of $CaSO_4$ in hot than cold water.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, THE SULPHATES, OF THIS GROUP.

74. *The metals* are heavier than water, and decompose it, at common temperatures, although Mg does so only slowly, with the formation of the oxides and evolution of H. Mg is nearly as volatile as Zn; the other three are not sensibly volatile. Ba, Sr, and Ca, oxidize on exposure to dry as well as moist air, but Mg oxidizes only in moist air. They dissolve easily in dilute HNO_3, H_2SO_4 and HCl, with disengagement of

---

* For another method for the separation and detection of these three substances, and for the photo-chemical method, the student is referred to pars. 99 and 101.

H; concentrated HNO_3 is almost without action on Sr, even when boiled upon it. They combine with Cl, I, Br, O, S, P, &c., at ordinary or more elevated temperatures. Mg unites directly with N; and when ignited in air or O it takes fire, burning with a dazzling light, which is remarkably rich in chemical rays, it is on this account employed for photographic purposes.

75. *The oxides* may be formed either by the ignition of their carbonates, nitrates, or any of their salts containing volatile acids, or by expelling the H_2O from their hydrates by heat. BaO, SrO, and MgO, *fuse* only at the very highest temperatures, as in the oxhydrogen blow-pipe flame, but even in this intense heat CaO exhibits no signs of fusing. These oxides are not reduced by H or by C. BaO, SrO, and CaO, when heated with S, are converted into a mixture of sulphate and sulphide, but MgO is not altered by it. Dry Cl converts them, with the exception of MgO,* at a full red heat into chlorides, with disengagement of O. BaO, SrO, and CaO, combine readily with H_2O, forming hydrates; the combination is attended with disengagement of heat. MgO combines only slowly with H_2O, and no sensible disengagement of heat attends the combination. These hydrates can also be prepared by dissolving one of their soluble salts in a boiling solution of NaHO; BaH_2O_2 is very frequently prepared by heating a solution of BaS with CuO. BaH_2O_2 is soluble in twenty times its weight of cold, and three times its weight of boiling, water; SrH_2O_2 is soluble in fifty times its weight of cold, and 2·4 times its weight of boiling, water; CaH_2O_2 dissolves in about 700 pts. of cold, and is less soluble in boiling, water; MgH_2O_2 is almost insoluble in water; the aqueous solutions of these hydrates have an alkaline reaction. In their dry state and in solution they attract CO_2 from the air and become converted into carbonates. When Cl is passed over them in

---

* MgO, Al_2O_3, and the other oxides termed earths, are not acted on by Cl, but if they are mixed with C they are then converted in an atmosphere of dry Cl into chlorides; the affinity of the C for the O, and the affinity of Cl for the metal effecting the transformation of these metallic oxides into chlorides.

their dry state, or into solutions of them, without the aid of heat, bleaching compounds (hypochlorites) are formed, thus :—

$$2CaH_2O_2 + 2Cl_2 = CaCl_2 + \underbrace{Ca2ClO}_{\text{Calcic hypochlorite.}} + 2H_2O.$$

They, like the alkalies, are converted by the Cl at higher temperatures into chlorates and chlorides. By the action of S upon the hydrates, a sulphide and an hyposulphite are formed, thus :—

$$3BaH_2O_2 + 2S_2 = 2BaS + BaS_2O_3 + 3H_2O.$$

76. The metals of this group furnish no other *basic* oxides but these.

77. *The sulphides* may be prepared by mixing their sulphates with C or carbonaceous matter, as starch, and subjecting the mixture to a strong heat, or by passing the vapour of CS_2 over the oxides in a state of ignition ; MgS, on account of its sparing solubility, may be prepared by adding a solution of K_2S to a solution of its sulphate. They are soluble, MgS only sparingly, in water, and are decomposed by it into sulphhydrates and hydrates of the oxides; the solutions possess an alkaline reaction. Exposed to the air, they absorb H_2O and CO_2, and are converted into carbonates with evolution of H_2S; they are also decomposed with evolution of H_2S by HCl, HNO_3, CO_2, &c. Heated in a current of air they are converted into sulphates ; in a current of Cl the chloride of the metal and chloride of sulphur are formed, in the moist state the chloride of the metal is also formed, but S is set free. If H_2S is passed into their solutions, they combine, forming hydric sulphides ($M''S,H_2S$) which are soluble ; these hydric sulphides are also obtained by passing H_2S into solutions of the oxides. CaS, H_2S, and MgS, H_2S, are decomposed by boiling H_2O into their hydric oxides and H_2S. A greater number of the sulphides than of the oxides of these metals have been formed.

78. *The chlorides* may be prepared by dissolving the oxides, their hydrates, the carbonates, or the sulphides, in dilute HCl; $BaCl_2$ may be obtained by fusing together 1 part of CaCl and 2 pts. of powdered native $BaSO_4$; $CaSO_4$ and $BaCl_2$ are formed,

and may be separated by treating the fused mass rapidly with boiling water. They are soluble in H_2O; $BaCl_2$ does not deliquesce in moist air, and is insoluble in absolute alcohol; the other three deliquesce in moist air, and are soluble in absolute alcohol; their aqueous solutions are neutral to test-paper; $CaCl_2$, from its extreme deliquescence, is frequently employed for desiccating substances. They all melt when heated; $Ca\,Cl_2$ and $Mg\,Cl_2$ melt at a low red heat. $Mg\,Cl_2$ is *partially* decomposed during the evaporation of its solution, HCl and MgO being formed; by adding NH_4Cl to the solution before commencing the evaporation, this decomposition is prevented, as a double chloride ($MgCl_2$, NH_4Cl) is formed, which does not lose acid on evaporation; $MgCl_2$ forms, as we see in this case, double chlorides with the alkaline chlorides. The chlorides of this group are not decomposed on being heated in a current of H.

79. *The nitrates* may be formed by dissolving the oxides, their hydrates, or the carbonates, in dilute HNO_3. They are soluble in water; $Ca(NO_3)_2$ and $Mg(NO_3)_2$ deliquesce in moist air, and are soluble in alcohol; the other two do not deliquesce, and are insoluble in alcohol. These nitrates are decomposed, as we have seen, by heat (75).

80. *The sulphates.*—$BaSO_4$ is insoluble in H_2O and in acids, but it is rendered notably soluble in H_2O by the presence of several salts, especially $MgCl_2$ and NH_4NO_3. $SrSO_4$ is sparingly soluble in H_2O, 1 pt. dissolving in 6895 pts. of H_2O; its solubility is *increased* by the presence of NaCl, and *decreased* by the presence of alkaline sulphates; or, if the water is acidulated with H_2SO_4, it is rather more soluble in dilute HCl and in dilute HNO_3 than in pure water. Ba and Sr are not completely precipitated from solutions containing metaphosphoric acid by H_2SO_4, and alkaline citrates impede their precipitation by H_2SO_4 in a high degree, but the precipitation appears on the addition of HCl. $CaSO_4$ is soluble in from 250 to 300 pts. of cold water; its *solubility* is increased if the water is acidulated with H_2SO_4, HCl, or HNO_3; its solubility is also increased in the presence of NH_4Cl, NaCl, and other sub-

stances; it is less soluble in hot than cold water. $Mg SO_4$ is readily soluble in water, is insoluble in absolute alcohol, and only slightly soluble in dilute spirit. The aqueous solutions of these salts do not alter vegetable colours. These sulphates, we have noticed, if mixed with C and strongly heated, are deoxidized. Heated to intense redness, $MgSO_4$ loses part of its acid, the other three are not altered at that heat. Solutions of the alkaline carbonates in the *cold* decompose $SrSO_4$, $CaSO_4$, and $MgSO_4$, but they have only a slight decomposing action in the cold on $BaSO_4$; but when boiling, and upon repeated application, they decompose completely this baric salt. These sulphates are also readily decomposed on being fused with alkaline carbonates.

81. *General characters of the salts of this group.*—The salts of these metals are colourless unless the acid is coloured. The soluble neutral salts are neutral or alkaline, not acid, to test-paper. The soluble baric, strontic, and calcic salts, with the exception of the chlorides, are decomposed upon ignition; all the soluble magnesic salts are decomposed, the sulphate partially, upon ignition, some of them even on the simple evaporation of their solutions. Most of the insoluble salts of this group are dissolved by dilute HCl. MgO differs from the other members, not only by its non-precipitation by $(NH_4)_2CO_3$ and by $(NH_4)_2C_2O_4$ in the presence of ammonic salts, but by the difficult solubility of its hydrate, and the ready solubility of its sulphate. A larger number of the salts of this group are insoluble than those of the first; the insolubility of the carbonates, phosphates, and oxalates, especially distinguish this group from the first; they are distinguished from the following groups by the solubility of their sulphides; they are therefore neither precipitated by $(NH_4)_2S$ nor by H_2S.

REMARKS ON THE INDIVIDUAL MEMBERS OF THE GROUP, WITH ADDITIONAL SPECIAL TESTS.

82. *Barium and its compounds.*—Ba, according to Davy, is

a silver-white metal, with less lustre than cast iron. According to Matthiesen, it is a powder of a yellow colour. BaO is a greyish-white friable mass. BaH_2O_2 is a white powder; it crystallizes from its solutions in colourless crystals, containing 8 at. of water of crystallization.

83. The principal minerals of Ba are the SULPHATE (*heavy spar*), and the CARBONATE (*witherite*).

84. H_2SiF_6 throws down, both from neutral and alkaline solutions of Ba, a white precipitate of $BaSiF_6$, which appears only after much agitation and the lapse of some time in dilute solutions; it is perceptibly soluble in HCl and in HNO_3. Addition of an equal volume of alcohol renders the precipitation rapid, and so complete that the filtrate remains clear upon addition of H_2SO_4.

85. If baric salts are held on the loop of a platinum wire in the hottest part of *Bunsen's gas flame*, the part of the flame above the sample is coloured YELLOWISH-GREEN. With the soluble baric salts, and also with baric carbonate and sulphate, the reaction is immediate, or very soon; but the phosphate, and also the silicates *decomposable by acids*, demand previous moistening of the sample with H_2SO_4 or HCl, by which means the Ba may be detected by the flame coloration. The silicates which HCl fails to decompose must be fluxed with Na_2CO_3, when the $BaCO_3$ produced will show the reaction. It is characteristic of the yellowish-green baric coloration of the flame that it appears bluish-green when viewed through the green glass. If the sulphates are selected, presence of calcic and strontic sulphates will not interfere with the reaction.—*Fresenius.*

Characteristic.—The reactions with $CaSO_4$, K_2CrO_4, and H_2SiF_6.

86. When O is passed over BaO at a dull red heat, they combine forming BaO_2 (baric peroxide), which is an indifferent body, and is decomposed at a bright red heat into BaO and O. Dissolved in H_2O acidulated with HCl, it is converted into $BaCl_2$ and H_2O_2 hydric peroxide.

87. *Strontium and its compounds.*—The colour of Sr is

yellow, darker in shade than that of Ca. SrO is a greyish-white powder or porous mass; SrH_2O_2 is also a greyish-white powder; it crystallizes from its solutions in transparent crystals containing 8 at. of water of crystallization.

88. The principal minerals of Sr are the SULPHATE (*celestine*) and the CARBONATE (*strontianite*).

89. H_2SiF_6 causes no precipitate in solutions of Sr; even upon addition of an equal volume of alcohol no precipitation takes place, except in very highly concentrated solutions.

90. $SrCl_2$ is soluble in alcohol; the solution burns with a *beautiful crimson flame*, which becomes more apparent on stirring the solution.

91. If a small particle of a strontic compound be introduced on the loop of a platinum wire into the flame of a *Bunsen's gas lamp*, it will impart an *intensely red colour* to the flame. As $SrCl_2$ gives the most intense coloration of all the strontic compounds, it is advisable, with all the other compounds, first to ignite them in the flame, then moisten with HCl, and again to introduce them into the flame. "Viewed through the *blue glass*, the strontic flame appears purple or rose (difference between Sr and Ca, which latter body shows a faint greenish-grey colour when treated in this manner); this reaction is the most clearly apparent if the sample moistened with HCl is let spirt up into the flame. In presence of Ba the strontic reaction shows only upon the first introduction into the flame of the sample moistened with HCl."

Characteristic.—The precipitation by $CaSO_4$ after the lapse of some time and the colour of the alcohol flame.

92. *Calcium and its compounds.*—The colour of Ca is light yellow. CaO and CaH_2O_2 are white powders.

93. The principal minerals of Ca are the SULPHATE (*gypsum, selenite*, $CaSO_4, 2H_2O$, *anhydrite* $CaSO_4$), the CARBONATE (chalk, limestone, marble, *arragonite, Iceland* or *calcareous spar*), the double CARBONATE OF LIME and MAGNESIA (*dolomite*, $CaCO_3$, $MgCO_3$), and the FLUORIDE (*fluor spar*, CaF_2).

94. H_2SiF_6 does not precipitate Ca from its solutions.

95. The alcoholic solution of $CaCl_2$ or $Ca(NO_3)_2$, when ignited, burns with a *yellowish-red coloured flame.*

96. *Ammonic arsenite* produces, in aqueous solutions of $CaCl_2$, an immediate precipitate of CALCIC ARSENITE. In solutions of $BaCl_2$ or $SrCl_2$ a precipitate is produced by this reagent only after the lapse of some time. Should this test be resorted to for confirming the presence of Ca, ammonic salts (if present) must first of all be removed from the solution, because the arsenites which are insoluble in water dissolve in it if ammonic salts are present.

97. If a small particle of a calcic compound be introduced on the loop of a platinum wire into the melting space of the flame of a *Bunsen's gas-lamp*, it will impart an orange-red colour to the outer flame. As $CaCl_2$ gives, of all the calcic compounds, the most intense coloration, it is advisable with all the other compounds to moisten them with HCl before introducing them into the flame. The coloration appears of a finch-green colour when viewed through the green glass, whilst the strontic flame, when viewed through the green glass, appears only of a weak yellow. In presence of Ba the calcic coloration shows only upon the first introduction of the substance into the flame.

Characteristic.—The non-formation of a precipitate on the addition of $CaSO_4$, and the formation of a precipitate on the addition of $(NH_4)_2C_2O_4$, and the coloration of the flame seen through the *green glass.*

98. Before describing the special properties of MgO we will give Fresenius's method for the separation and detection of BaO, SrO, and CaO (par. 99), and also the photo-chemical method (par. 101).

99. Dissolve the precipitate produced by the group reagent $(NH_4)_2CO_3$, after it has been well washed in the least possible quantity of HCl, and add to *a small portion of the fluid* some solution of $CaSO_4$ (not too little); *a precipitate is formed immediately*;* Ba is, and Sr and Ca may be, present.

---

* If a precipitate is not formed immediately, but only after the lapse of some time, examine the other portion of the solution according to 70; if

100. Evaporate the remainder of the HCl solution to dryness, digest the residue with *absolute* alcohol, which dissolves $SrCl_2$ and $CaCl_2$, but leaves the greater part of the $BaCl_2$ undissolved, filter after having moistened the filter with alcohol, dilute the filtrate with an equal volume of H_2O, mix with a few drops of H_2SiFl_6, let the mixture stand several hours to allow time for the trace of $BaSiF_6$ to precipitate, then filter and add dilute H_2SO_4 to the alcoholic filtrate; the Sr and Ca will be precipitated as sulphates; filter and wash the precipitate with weak alcohol, then boil the precipitated sulphates in a solution of Na_2CO_3; $SrCO_3$ and $CaCO_3$ will be formed. Filter, wash the precipitated carbonates with distilled water, then dissolve them in HCl, evaporate the solution to dryness, and dissolve the residue in a small quantity of water and examine for Sr and Ca as directed in par. 71 after the Ba has been removed.

101. "The three alkaline earths may be detected in mixtures containing all three of them by the different coloration which they severally impart to the flame. To this end the sample under examination is repeatedly moistened with H_2SO_4, then cautiously dried, and introduced into the fusion zone of the gas flame. After the evaporation of the alkalies that may chance to be present, the baric coloration will make its appearance alone. After this coloration has completely disappeared, and the sample moistened with HCl gives on spirting no longer a flame coloration of a bluish-green tint when viewed through the green glass, the sample is moistened again with HCl and tested for Ca by viewing it through the green glass when spirting, for Sr by viewing it under the same circumstances through the blue glass."—*Fresenius.*

102. *Magnesium and its compounds.*—Mg is the colour of silver; MgO and MgH_2O_2 are white powders.

103. Mg is found in nature principally in the state of SULPHATE (*Epsom salts*, $MgSO_4$, $7H_2O$) of carbonate, chloride

---

no precipitate is formed, examine the other portion of the solution according to 69.

(see par. 43), and in combination with silicic acid in various proportions, forming the *meerschaum*, *serpentine*, &c.

104. NH_4HO precipitates from aqueous solutions of magnesic salts a portion as MgH_2O_2, the rest of the Mg remains in solution as a double salt with the ammonic one produced.

105. The *fixed alkalies* and the other *alkaline earths* precipitate Mg from its solutions as MgH_2O_2, which is soluble in ammonic salts; their addition, therefore, either before or after the precipitation, prevents or redissolves the precipitate of MgH_2O_2.

106. $(NH_4)_3AsO_4$ produces in neutral or alkaline solutions of Mg a precipitate of $MgNH_4AsO_4$, which is soluble in acetic and other weak acids.

107. Na_2HPO_4 produces in concentrated neutral solutions of Mg a precipitate of $MgHPO_4$. A magnesic phosphate more insoluble in H_2O may be produced by adding, before the Na_2HPO_4, NH_4Cl and NH_4HO; in this case the precipitate is $MgNH_4PO_4$. Both these magnesic phosphates are soluble in acids.

108. According to the experiments of Dr. Divers, $(NH_4)_2CO_3$, other ammonic salts being absent, precipitates Mg completely from its solutions after the lapse of some time, the precipitation commencing to form a few minutes after the addition of the reagent. The precipitate is $MgCO_3$, unless 4 eq. of $(NH_4)_2CO_3$ is added to every one of the magnesian salt; in that case the precipitate is $MgCO_3, (NH_4)_2CO_3$. When NH_4Cl is present, the simple carbonate ($MgCO_3$) never precipitates, it is always the double carbonate; and when the NH_4Cl is added in the proportion of 2 eq. to every one of the magnesic salt, the precipitate does not begin to form until about a quarter of an hour after the addition of the $(NH_4)_2CO_3$, and even after the lapse of twenty-four hours the precipitation of the Mg is not complete. The ammonic magnesic carbonate is more soluble in H_2O than in solutions of NH_4Cl or $(NH_4)_2SO_4$, and it is almost totally insoluble in solutions of $(NH_4)_2CO_3$.

109. If magnesic compounds, after being ignited strongly

by the blowpipe flame upon a charcoal support, be moistened with a solution of $Co(NO_3)_2$, and again ignited, the mass assumes, on cooling, a pale *flesh colour.*

110. Magnesic salts impart no colour to the flame.

Characteristic.—The reactions with the soluble phosphates and arseniates, and with $Co(NO_3)_2$.

111. Answers to the following exercises must be written out.

EXERCISES.

19. In what state is Ba, Sr, Ca, and Mg, met with in nature?

20. Do you know any baric salt which is insoluble in acids?

21. Mention the similarity and dissimilarity in properties of the metals of this group?

22. Why are you directed to dissolve the precipitated carbonates of the 1st division in acetic acid? Why not dissolve them in HCl?

23. I have some baric sulphate, and I wish to prepare some baric hydrate in solution: how am I to proceed?

24. By what single reagent and in one operation can the absence of Ba and Sr be discovered?

25. Describe the action of Cl upon CaH_2O_2 at the common temperature, at the temperature of boiling water, and at a red heat.

26. How can Ca be detected in the absence of Ba and Sr?

27. Are the oxides of the metals of the alkalies and alkaline earths reducible by H or C?

28. How can Sr be detected in the absence of Ba?

29. Can the presence or absence of Ca be determined as long as Sr remains in solution?

30. If a solution of baric, strontic, or calcic hydrate is exposed to the air it becomes covered with a film: explain the cause of this.

31. Can the presence or absence of Ca and Sr be determined as long as Ba is present in a solution?

32. How is fluoride of silicon prepared? Illustrate by symbols the changes which take place in passing it into water.

33. What occurs when BaO, SrO, CaO, or MgO, is treated with S?

34. Why does the addition of NH_4HO to a solution of a baric, strontic, or calcic salt, to which a solution of $H_2\bar{O}$ has been previously added, *promote* the formation of the precipitate?

35. Describe as many methods as you are able for distinguishing Ba, Sr, Ca, when they occur in the same solution.

36. What is the action of reagents on solutions of Mg?

37. If you had a solution to examine for the members of the 1st and 2nd groups, and from its nature you were certain that baric and strontic compounds were absent, what reagent would you employ to detect and separate the Ca, if present, from Mg and the alkalies?

38. How would you prepare baric carbonate from the sulphate?

39. Supposing you had a solution containing an alkaline carbonate, how could you ascertain qualitatively whether it contained any free alkali?

40. From your knowledge of Berthollet's laws, what would you infer would be the result of adding a solution of BaH_2O_2 to an aqueous solution of a magnesic salt?

41. If an oxalate of Ba, Sr, or Ca, was dissolved in an acid, and NH_4HO were added in excess to the acid solution, what would be the effect?

42. Among the impurities contained in coal gas are, as already noticed $(NH_4)_2CO_3$, $(NH_4)_2S$, CO_2, and H_2S. The gas is frequently made to pass through calcic hydrate: does the hydrate effect any change in these impurities? Illustrate your answer by equations.

43. How is hydric peroxide prepared?

THIRD GROUP.

ZINCIC OXIDE (ZnO), MANGANOUS OXIDE (MnO), NICKELOUS OXIDE (NiO), COBALTOUS OXIDE (CoO).

Solutions for the reactions:—$ZnSO_4$, $MnCl_2$, $NiSO_4$, $CoSO_4$, in water.

112. *Examination for the members of the group.*—When a solution is examined for this group *only*, *the group reagent* $(NH_4)_2S$ must be added as directed at par. 366, and the precipitate, after being well washed with water containing a little $(NH_4)_2S$, must be examined, if it is of a *light colour*, according to par. 113; if it is of a *black colour*, according to par. 114.

113. As the precipitate is of a *light colour*, Ni and Co must be absent (J 1, K 1). Examine it for Mn by the blowpipe test; if Mn is *absent*, examine it for Zn by the blowpipe test. *When* Mn *is present*, dissolve it in as small a quantity of *boiling dilute* HCl as possible;* boil to expel H_2S,† then add $(NH_4)_2CO_3$ in excess and boil for some time; the Mn will be precipitated as $MnCO_3$ (G 3), whilst Zn, if present, will remain in solution. Filter, and to the filtrate add $(NH_4)_2S$, when Zn, if present, will be precipitated as sulphide; confirm its presence by dissolving the precipitate, after it has been well washed, in hot dilute HNO_3, adding to it a small quantity of a solution of $Co(NO_3)_2$ (not even enough to impart a pink colour), then a solution of Na_2CO_3 in slight excess; the solution must then be boiled for a minute or two and the precipitate afterwards collected on a filter and washed; the filter with the precipitate is then incinerated on platinum foil. The

---

* In order to use as little acid as possible, pour the boiling acid in small quantities at a time upon the precipitate collected upon the filter. If the precipitate be very large, remove it from the filter into an evaporating dish before adding the acid.

† To ascertain when all the H_2S is expelled, hold a piece of bibulous paper, moistened with a solution of some soluble lead salt, over the boiling liquid; when the lead paper does not alter in colour, all the H_2S is expelled.

TABLE III.

BEHAVIOUR OF THE THIRD GROUP WITH THE SPECIAL REAGENTS.

MnO.	ZnO.	CoO.	NiO.
G 1. MnS is *flesh-coloured,* but becomes *brown* on exposure to the air; soluble in the weak acids, as acetic, as well as in the dilute mineral acids.	H 1. ZnS, like the oxide, is white; insoluble in acetic acid, but dissolves in the dilute mineral acids.	J. 1. CoS is *black;* insoluble in the dilute mineral acids, as well as in the weaker acids. Soluble in nitro-hydrochloric acid.	K 1. NiS is *black;* insoluble in the dilute mineral acids, as well as in the weaker acids. Soluble in nitro-hydrochloric acid.
G 2. The *fixed alkalies* precipitate from solutions of Mn, MnH_2O_2, which is of a whitish colour at first, but speedily becomes blackish-brown on exposure to the air; *it is insoluble in an excess of either of the fixed alkalies.* The presence of ammonic salts prevents in a great measure the precipitation.	H 2. The *fixed alkalies* precipitate from solutions of Zn, ZnH_2O_2, which is white; *it is completely soluble in an excess of either of the fixed alkalies, if the alkali is perfectly free from carbonate.*	J. 2. The *fixed alkalies* precipitate from solutions of Co, *blue basic salts,* which turn *green* on exposure to the air; and are converted, upon boiling, into the PALE RED HYDRATE, which is generally discoloured, owing to a little Co_2O_3 being formed. *Each of these precipitates is insoluble in an excess of either of the fixed alkalies.*	K 2. The *fixed alkalies* precipitate from solutions of Ni, NiH_2O_2, in the form of a *light green precipitate,* which is unalterable in the air, and *insoluble in an excess of either of the fixed alkalies.*
G 3. $(NH_4)_2CO_3$ produces in solutions of Mn a precipitate of $MnCO_3$, which is white, *and insoluble in an excess of the reagent,* especially on boiling.	H 3. $(NH_4)_2CO_3$ produces in solutions of Zn a precipitate of *white* BASIC CARBONATE OF ZINC, which is easily soluble in an excess of the reagent.	J. 3. $(NH_4)_2CO_3$ produces in solutions of Co a *red* precipitate of CARBONATE OF COBALT, which is *readily soluble in an excess of the reagent,* the solution having a red colour.	K 3. $(NH_4)_2CO_3$ produces in solutions of Ni an *apple-green* precipitate of *carbonate of nickel,* which is *readily soluble in an excess of the reagent,* the solution having a greenish blue colour.

The alkalies fail to precipitate the members of this group in the presence of non-volatile organic matter, such as starch, sugar, tartaric acid, &c.

green colour is very bright if an excess of cobalt be *avoided*, and is best seen after the gritty residue has been powdered under a glass rod.—*Bloxam.*

114. The precipitate is *black;* all the members of the group must therefore be sought for. Examine a portion of the precipitate for Mn by the blowpipe test. Treat the rest of the precipitate, whether Mn is present or not, with *cold dilute* HCl; NiS and CoS will remain undissolved, whilst MnS and ZnS will dissolve; examine the acid solution according to par. 115, and the undissolved portion according to par. 116.

115. Boil the filtered HCl solution, which may contain Mn and Zn, until all H_2S is expelled (see second note, page 41), then add a solution of one of the *fixed alkalies in excess*; Mn* will be precipitated, whilst Zn will remain in solution; filter if the alkali has produced any precipitate, and add to the filtrate or to the solution (when it does not require filtering)

---

* It is almost impossible to prevent a minute quantity of CoS and NiS oxidizing, even if the precipitate is washed most carefully with water containing $(NH_4)_2S$; the oxidized portion of these two bodies will, therefore, be present in the HCl solution, and consequently be precipitated by the fixed alkali; a precipitate may, therefore, be produced by the alkali, when no Mn is present. It will not be necessary to examine this precipitate for Ni and Co, as sufficient will remain undissolved, unless the student has allowed the $(NH_4)_2S$ precipitate to remain on the filter for a great length of time.

KHO and NaHO solutions very frequently blacken slightly on the addition of H_2S from their containing small traces of oxides of iron and copper; it is therefore necessary before employing the alkali solution to examine it for these oxides; if one or both of them are present the precipitate produced by H_2S must be redissolved in a few drops of dilute HNO_3, and if Cu as well as Fe is present H_2S must be passed through the solution until it is in excess, the liquid must then be filtered, and the filtrate boiled in an evaporating dish with a few drops of HNO_3 until all the H_2S is expelled and the Fe has become peroxidized, NH_4HO is then added in excess, the liquid filtered, and to the filtrate must be added $(NH_4)_2S$, which will produce a white precipitate if Zn is present. If the alkali solution does not contain Cu, but only Fe, after the solution of the precipitate in HNO_3, NH_4HO is at once to be added in excess, and the filtrate from the NH_4HO precipitate tested for Zn with $(NH_4)_2S$.

H_2S, when Zn, if present, will be precipitated; confirm its presence as directed at par. 113.

116. After having washed the black residue, examine it for Ni and Co in the following way:—Expose a small portion of it on a bead of borax to the outer blowpipe flame, in the way directed in par. 152. A blue bead denotes the presence of Co; this is a safe and certain test for Co; consequently, if a blue bead is not produced, Co is absent. If a yellow, and not a blue bead has been formed, which become grey and dull in the inner flame, Ni is present. When Co is present, Ni is sought for in the following way:—The remainder of the precipitate is dissolved in aqua regia, and the acid solution evaporated almost to dryness; a concentrated solution of KCy is then added in excess, and the whole solution must then be boiled for some time, adding a little water from time to time, to replace that which evaporates. To the solution, which must not be filtered even if a precipitate has been formed, is added, when it is cold, H_2SO_4 slightly in excess; if in some hours after the acid has been added a precipitate appears, Ni is present; if no precipitate appear, or at least only a crystalline one which redissolves in water, Ni is absent.

117. Ni may also be detected in the presence of Co by the two following methods. 1st method:—"The acid solution which contains Co, and which may contain Ni, must be evaporated nearly to dryness, KNO_2 must then be added in not too small a proportion, and acetic acid to strongly acid reaction, let the mixture stand for at least several hours in a moderately warm place, when Co will separate as nitrate of sesquioxide of cobalt and potash; the Ni may then be readily precipitated from the filtrate by NaHO or $(NH_4)_2S$. 2nd method:—Saturate with Cl the very dilute solution of the two metals in HCl, having the acid slightly in excess; add $BaCO_3$ in excess, and let the fluid stand twenty-four hours. The Co is entirely precipitated in this process as black sesquioxide, whilst the Ni remains in solution, and may, after the removal of the Ba by H_2SO_4, be precipitated by solution of NaHO.

118. *The following precautions are to be attended to in the*

analysis of this group:—When Mn is present, care must be taken to expel all the H_2S from the HCl solution, before $(NH_4)_2CO_3$ is added to separate the Mn from the Zn. Before adding H_2SO_4 to the KCy solution, it will be better to add a little water, in order to prevent any K_2SO_4 from crystallizing out, which might mislead the student as regards Ni. On adding NaHO to the HCl solution, which may contain the Zn and Mn and small traces of Ni and Co, from the partial oxidation of their sulphides, a small precipitate will frequently be formed, if only Zn be present. This is occasioned by the caustic alkali having absorbed some CO_2 from the air, and become partially converted into carbonate, which causes a partial precipitation of the Zn.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, THE SULPHATES, OF THIS GROUP.

119. *The metals.*—Zn melts at 412° C., and at a bright red heat volatilizes; the other three metals are almost as infusible as Fe. In damp air Mn gradually crumbles down to a brown oxide, Zn is tarnished, the other two are less affected by it than Fe; they all combine with O on exposure to air or O, at a red heat, the combination with Zn being attended with flame. Mn decomposes water slowly at common temperatures; the other three decompose it at a red heat, with disengagement of H. They dissolve in dilute H_2SO_4 and in HCl, H being evolved, and salts of the metals formed. HNO_3 oxidizes and dissolves them, a nitrate of the metal being formed. The gaseous compound formed in the case of Co and Ni is NO_2,; N_2O is one of the gaseous products when Zn is acted upon by dilute acid. The gaseous body formed depends in this, as in other cases, on the strength of the acid and the temperature, for if Zn be acted upon by undilute HNO_3, NH_3 is one of the products. These two reactions are represented in the following equations:

$$(1)\ 4Zn + 10HNO_3 = N_2O + 4(Zn2NO_3) + 5H_2O$$

$$(2)\ 4Zn + 9HNO_3 = NH_3 + 4(Zn2NO_3) + 3H_2O$$

If an excess of acid be employed, it, or a portion of it, combines, of course, with the NH_3 formed in the second reaction. Zn decomposes CO_2 at a red heat; it dissolves in boiling KHO, H being evolved; thus, $Zn + 2KHO = K_2O, ZnO + H_2$.

Co and Ni are magnetic; the Ni loses this property almost entirely if heated to a point exceeding 332° C., but recovers its magnetic power on cooling.

120. *The oxides* may be obtained by igniting the hydrates or carbonates out of contact of the air; they are non-volatile, and are not decomposed by heat alone; they may be reduced to the metallic state by ignition with C, or, with the exception of Mn, on being heated in a current of H or CO. On being heated with NH_4Cl, CoO and NiO are reduced to the metallic state, but ZnO and MnO are left by it in the state of chlorides. On being heated in contact with air, ZnO and NiO suffer no change, but MnO and CoO are converted into Mn_3O_4 and Co_3O_4. ZnO, CoO, and NiO, on being heated with S, are converted into sulphides, SO_2 being evolved; in the case of MnO an oxysulphide is formed. Heated in a current of Cl, they are converted into chlorides, O being evolved. *The hydrates* are obtained by adding to solutions of their salts one of the fixed alkalies, as shown in Table III. ZnO and ZnH_2O_2 are *white;* ZnO, when heated, turns *lemon-yellow,* and on cooling turns *white* again; MnO is *greyish*-green, MnH_2O_2 is *white;* both absorb O from the air, and become converted into *brown* Mn_2O_3HO. NiO is *greyish-green;* NiH_2O_2 is *green;* CoO is an *olive-green;* CoH_2O_2 is *pale red.* These oxides and hydrates are in the form of powders, and are insoluble in H_2O, but dissolve readily in HNO_3, HCl, and H_2SO_4. ZnO and its hydrate are soluble in the alkalies, CoO and NiO and their hydrates in the volatile alkali, and MnO and its hydrate in NH_4Cl. If Cl is passed through H_2O in which MnO, NiO, or CoO, or their hydrates, are suspended, a part of the metal is precipitated in the state of $M_2H_6O_6$, and the remainder remains in solution as MCl_2, if the liquid, in which the oxides or the hydrates are suspended, is strongly *alkaline* the *whole* of the Co

and Ni are converted into the hydrates of the sesquioxides $Co_2H_6O_6$ and $Ni_2H_6O_6$, and the Mn is converted into the hydrated MnH_4O_4.

121. *The sulphides* are obtained in the *hydrated* state by adding to a solution of their salts an alkaline sulphide, or by passing into their alkaline solutions H_2S; their *colour* and their solubility in acids are noticed in Table III. They are insoluble in H_2O in the alkalies and alkaline sulphides, with the exception of NiS, which, under certain circumstances, dissolves to a slight extent in the alkaline sulphides, imparting thereby to the solution a brownish colour. H_2S causes no precipitate in solutions of these metals containing free mineral acids, but it precipitates completely Zn from the solution of the acetate, even if free acetic acid is present. In neutral solutions H_2S does not completely precipitate the metals as hydrated sulphides, the solutions of zincic, cobaltous, and nickelous acetates excepted. They all oxidize more or less on exposure to air. SO_2 converts MnS and ZnS into hyposulphites, but it dissolves only sparingly the other two. Heated out of contact with air, they are converted into anhydrous sulphides, H_2O being expelled. In the anhydrous state ZnS is of a yellowish colour, MnS is green, NiS bronze yellow with metallic lustre, CoS is grey with metallic lustre. In the anhydrous as well as in the hydrated state they are decomposed more or less readily when heated in a current of Cl, metallic chlorides being formed, and chloride of sulphur* evolved. Roasted in air, they are converted into oxides with evolution of SO_2. The hydrated sulphide of Mn precipitates Co as CoS from solutions of its salts, and the hydrated sulphides of Mn and Co precipitate Ni from the solutions of its salts, and Fe from Fe_2Cl_6, Pb from $Pb(\bar{A})_2$, Cu from $CuSO_4$, and Ag from $AgNO_3$, as sulphides.

122. *The chlorides* may be obtained by dissolving the metals, the anhydrous or hydrated oxides or carbonates in HCl, or by dissolving in this acid by the aid of heat any of the higher oxides of Mn, Co, or Ni; in these latter cases Cl is evolved.

---

* There are two chlorides of sulphur, S_2Cl_2 and SCl_2; they are decomposed by water into SO_2, HCl, and S.

On evaporating the solutions obtained by any of these modes, the salts are obtained crystallized and hydrated, thus—$ZnCl_2H_2O$,* $MnCl_24H_2O$, $CoCl_26H_2O$, $NiCl_29H_2O$. They may be obtained in the anhydrous state by igniting the hydrates, or by heating the metals in a current of Cl; in the anhydrous state they all attract moisture from the air, but the first two deliquesce in the hydrated state. $MnCl_2$ and $ZnCl_2$ melt at a dull red heat; at higher temperatures they sublime, and the latter can be distilled; the other two may sublime without first fusing; if ignited in the air above the fusing point $MnCl_2$, if the ignition is protracted, becomes converted into oxide, and the others lose more or less Cl, a corresponding quantity of oxide being formed. Heated in PH_3, they are converted into phosphides, HCl being evolved; and with the exception of $MnCl_2$ they are reduced to the *metallic* state when heated to redness in a current of H. If Cl is passed through solutions of $MnCl_2$ and $CoCl_2$, they are converted into Mn_2Cl_6 and Co_2Cl_6, and on the subsequent addition of $BaCO_3$, Mn_2O_3 and Co_2O_3 are precipitated.

123. The *nitrates* may be obtained by dissolving the metals in HNO_3, or the anhydrous or hydrated oxides or the carbonates in the acid diluted; they are soluble in H_2O, and on evaporating their aqueous solutions crystallized hydrated salts are obtained; they are decomposed on ignition, a higher oxide of Mn, Ni, and Co, than the monoxide being left.

124. *The sulphates* may be obtained by dissolving the metals, the anhydrous or hydrated oxides, or the carbonates in dilute H_2SO_4; or by heating the higher oxides of Mn, Ni, Co, in undilute acid, and $ZnSO_4$ may be prepared by gently roasting in the air zinc blende. They are soluble in H_2O, and crystallize from their aqueous solutions on evaporation, $MnSO_4$ with 5 atoms,† and the other three with 7 atoms, of H_2O. On

---

* $ZnCl_2$ in solution, under the name of Burnett's Disinfecting Fluid, has been extensively used as an antiseptic and as a preservative of wood and vegetable fibre.

† $MnSO_4$ crystallizes below 42° with 7 ats. of H_2O, and between 45° and 68° with 5 atoms, and between 68° and 86° with 4 atoms.

being heated the water is expelled, and they are left in the anhydrous state; they bear a moderately strong red heat without decomposing, but at a bright red heat they are decomposed, the metals being left in the state of oxides, higher oxides than the monoxides in the case of Mn, Ni, and Co.

125. *The general characters of the salts of this group.*—The zincic salts, in the anhydrous and hydrated states are *white;* the manganous salts are *white* or *red;* most of the nickelous salts are *yellow* in the anhydrous, and *green* in the hydrated, state, their *solutions* are of a *light green* colour; the cobaltous salts are *red* in their hydrated, and mostly *blue* in their anhydrous, state, *their solutions*, even when much diluted, have a delicate *rose tint;* the *red* solution of $CoCl_2$ on evaporation turns *blue*, or on the addition of strong mineral acids to its solutions. The neutral salts of these metals, soluble in water, are decomposed by heat, the sulphates being the least decomposable; the manganous soluble neutral salts are *neutral*, and the soluble neutral salts of the other three metals are *acid*, to litmus paper. Zincic and manganous compounds, which are insoluble in H_2O, dissolve in HCl; and *most* of the nickelous and cobaltous compounds, which are insoluble in H_2O, are soluble in HCl. $BaCO_3$, or $CaCO_3$ does not precipitate the oxides from aqueous solutions of the salts upon digestion in the cold, *with the exception of the sulphates;* but if the solution has been treated with Cl or Br, Mn and Co are precipitated from their salts by these carbonates, as Mn_2O_3 and Co_2O_3. A solution of Na_2CO_3 precipitates from

The sulphates of Mg, Zn, Mn, Co, Ni, and Fe are isomorphous; they usually crystallize with 7 ats. H_2O, but under certain conditions with 6, and cupric sulphate, which belongs to the group, never contains more than 5; they sometimes crystallize with 4 and sometimes even with 2. These sulphates, which are frequently termed magnesian sulphates, retain 1 at. H_2O with considerable force, and it can be replaced by an anhydrous sulphate, as K_2SO_4; these double sulphates, even the double cupric sulphate, always crystallize with 6 ats. H_2O. This atom of water was called by Graham constitutional water.

solutions of the *normal* salts of Co, Ni and Zn, as it does also from similar salts of Mg and Cu, not a normal, but a basic, carbonate. The members of this group are distinguished from those of the preceding by the insolubility of their oxides and sulphides in H_2O, and from those of the next group by their behaviour with NH_4HO.*

REMARKS ON THE INDIVIDUAL MEMBERS OF THE GROUP, WITH ADDITIONAL SPECIAL TESTS.

126. *Mn and its compounds.*—Mn is greyish white, very brittle, and melts only at the strongest heat of a blast furnace.

127. The most important and most valuable ore of Mn is the peroxide (MnO_2); it is employed for obtaining Cl from HCl.

128. NH_4HO precipitates from solutions of manganous salts part of the Mn as $Mn H_2O_2$, which an excess of the reagent does not redissolve; but NH_4HO produces no precipitate in the presence of NH_4Cl, or any ammonic salt the acid of which forms no insoluble salt with Mn. An ammonic solution of Mn rapidly attracts O from the air, one of the higher oxides of Mn being formed, which is insoluble in NH_4HO, and therefore precipitates as quickly as it is formed, and in brownish flocks.

129. If a few drops of a fluid containing a manganous compound, and free from Cl, are sprinkled on PbO_2 or Pb_3O_4, and HNO_3 free from Cl is then added, and the mixture boiled and allowed to settle, the $Mn(NO_3)_3$ formed, imparts a *purple red* colour to the fluid.

130. The smallest quantity of Mn can be detected in any of its compounds, by fusing them, in conjunction with Na_2CO_3

---

* Cobaltous and nickelous oxalates are nearly insoluble in water and in a solution of oxalic acid, but they are soluble in NHHO; on exposing to the air an ammonic solution of the two oxalates for several days, the nickelous oxalate is deposited, whilst the cobaltous oxalate remains in solution.

and a small quantity of KNO_3, upon platinum foil or wire, in the outer blowpipe flame; sodic manganate (Na_2MnO_4), which is of a bluish green colour, being produced,* which, on being dissolved in H_2O yields a *green* solution, turning *red* on the addition of acetic acid, and often afterwards becoming colourless, with separation of brown flocculi. "This method fails to detect manganese in limestone rocks, on account of the insolubility of the lime salt in Na_2CO_3 and KNO_3; but if, along with the two reagents just mentioned, a little borax be added, so as to attack and dissolve a portion of the mass, the well-known greenish blue enamel is quickly produced."—*Chapman.*

Characteristic.—The reactions with $(NH_4)_2S$, PbO_2 and the blowpipe test.

131. Five other oxides of Mn are known—Mn_2O_3, feebly basic, is found in nature in the anhydrous and hydrated states; it may be formed by exposing MnO or MnH_2O_2 to air, or by passing Cl, not to saturation, through H_2O in which MnH_2O_2 or $MnCO_3$ is suspended. Mn_3O_4 is found in nature; the other oxides of Mn are converted into this one by igniting them in the air. MnO_2 is found in nature in the anhydrous and the hydrated state; this and the previous oxide are indifferent bodies; MnO_2 is left in the hydrated state when Mn_3O_4 is treated with HNO_3. The two next are acid bodies; they cannot exist except in combination, with H, or a metal; the general formula of their salts is M_2MnO_4, $M_2Mn_2O_8$. The first are termed manganates and the latter permanganates; they are formed by fusing MnO_2 with KHO. Each of these oxides is converted into $MnCl_2$, with evolution of Cl on being heated with HCl.

132. *Zn and its compounds.*—Zn is a hard, bluish-white metal; it is rather brittle at ordinary temperatures, but between

---

* The manganates and permanganates, especially the latter, are employed as oxidizing and disinfecting agents; under the name of *Condy's fluid* they are largely used for these purposes.

Before making the blow-pipe experiments, consult the pars. under the head "Blow-pipe" in Part III.

94° and 149° C., it possesses considerable ductility and malleability; at a little higher temperature it again becomes so brittle that it may be powdered in a mortar. Zn is a constituent of several alloys; brass, pinchbeck, muntz or yellow metal, ***hard solder*** for brass are alloys of Cu and Zn; other alloys we shall notice under the other metals.

133. The principal minerals of Zn are the anhydrous CARBONATE (calamine, $ZnCO_3$) and the SULPHIDE (Zinc blende ZnS).

134. When compounds of Zn, mixed with Na_2CO_3, are subjected upon a charcoal support to the inner blowpipe flame, Zn is produced, which volatilizes, and, on passing through the oxidizing flame, becomes again converted into oxide. The charcoal support becomes encrusted with this oxide, which is of a yellow colour while hot, and turns white on cooling.

135. If a compound of Zn be moistened with $Co(NO_3)_2$ and exposed on charcoal to the outer blowpipe flame, a mass of a beautiful green colour will be produced; the colour is best seen when the mass has become cold.

136. (*a*) "*Reduction-film* black, in the thin parts brown.

(*b*) "Oxide-film white, and therefore invisible. To test it, a square centimètre of filter-paper moistened with HNO_3 is rubbed over the surface and then rolled up on two rings on fine platinum wire, three millimètres in diameter, and burnt. If the paper is burnt in the upper oxidizing flame at as low a temperature as possible, the ash forms a small solid mass about a square millimètre in area, which can be ignited without fusion, and becomes yellow on gently heating, and appearing white on cooling. If this be moistened with a few milligrammes of very dilute $Co(NO_3)_2$ solution and ignited, it appears of a beautiful green colour on cooling; the same reaction can be effected with the metallic-film."—*Bunsen.*

Characteristic.—The reactions with KHO, $(NH_4)_2S$ and the blowpipe test.

137. Zn forms only one oxide, so far at least as is at present known.

138. *Ni and its compounds.*—Ni is a brilliant, silver-white,

hard but ductile metal; it surpasses Fe in tenacity. It may be obtained pure by heating the oxalate intensely in a crucible with a luted cover. The principal ore of Ni is copper-nickel (NiAs). NiO yields insoluble compounds with K_2O, Na_2O, BaO, SrO, and several other bases; some of them are decomposed by frequent washings with boiling water. German silver, packfong and tutenag (a Chinese alloy), are alloys of Ni, Zn, and Cu.

139. NH_4HO, added in small quantity to solutions of Ni, produces in them a trifling greenish turbidity; upon further addition of the reagent, this redissolves readily to a blue fluid, containing a compound of oxide of nickel and ammonia.

140. KCy throws down from solutions of Ni a yellowish-green precipitate of $NiCy_2$, which redissolves in an excess of the precipitant as $NiCy_2$, 2KCy; the solution is brownish-yellow, on the addition of HCl or H_2SO_4 to this solution $NiCy_2$ is reprecipitated, whilst the KCy is decomposed, HCy being evolved; the $NiCy_2$ is very difficultly soluble in an excess of either of the acids in the cold, but more readily upon boiling.

141. KNO_2, used in conjunction with acetic acid, fails to precipitate Ni even in concentrated solutions.

142. In the exterior flame of the blowpipe, nickel compounds impart to beads of borax a reddish-yellow tint; the colour fades upon cooling, and finally disappears almost entirely. If exposed with borax to the inner flame, the bead becomes grey; if a minute fragment of KNO_3 be added to the bead after exposure to the inner flame, and it is then fused in the outer flame, it acquires a rich purple colour.

143. "*Reduction on charcoal splinter.*—On pulverizing the charcoal white, lustrous, ductile, metallic particles are obtained, forming a brush on the magnetized blade. The metal dissolved in HNO_3 on paper gives a green solution, which on moistening with soda, exposure to bromine vapour, and subsequent addition of soda, gives a brownish-black spot of Ni_2O_3. The ash of the paper, from which the excess of soda has been washed out, can be used for the borax-bead test."—*Bunsen.*

144. *Borax-bead.*—" Oxidizing flame greyish-brown, or dirty violet. Upper reducing flame grey, from reduced Ni, which often collects to a spongy mass of metal, rendering the bead colourless."—*Bunsen.*

Characteristic.—The reactions with NH_4HO, KCy, and the blowpipe test.

145. There is one other oxide of Ni known, viz. Ni_2O_3; it forms no salts, and is converted on being heated with acids into nickelous salts; it may be obtained by digesting NiH_2O_2 with Cl, or with an alkaline hypochlorite.

146. *Co and its compounds.*—Co is hard and of a reddish-grey colour. The principal minerals of this metal is the TIN-WHITE COBALT, or SMALTINE ($CoAs_2$), and the bright white cobalt, or cobalt glance (CoS_2, $CoAs_2$).

147. " CoO combines with bases as well as with acids. If fused with KHO it forms a *blue* compound, which is decomposed by the free addition of H_2O; when heated with $Mg(NO_3)_2$ a pale *pink* residue is obtained, a combination of MgO and CoO; with Al_2O_3, it forms the blue pigment known as Thénard's blue, and with ZnO the compound known as Rimner's green." This, and other oxides of Co, on being treated with ammonia, unite with it forming ammonio-cobalt bases of complex constitution. Characters traced on paper with a dilute solution of $CoCl_2$, are invisible in the cold, but become blue by heat, and again fade in the cold as the hygroscopic moisture of the paper is restored. The chief use of cobalt in the arts is in the production of Smalt's (powdered blue glass), Thénard's blue, Rimner's green, and other pigments.

148. NH_4HO produces in solutions of cobaltous salts the same precipitate as the fixed alkalies do; but the precipitate is soluble in an excess of NH_4HO, the ammonic solution having a reddish-brown colour: the fixed alkalies produce no precipitate, or at least a very slight one, in the ammonic solution. NH_4HO causes no precipitate, if NH_4Cl is present.

149. KCy precipitates from *acid* solutions of cobalt salts a brownish-white cobaltous cyanide $CoCy_2$, dissolving easily in an excess of the precipitant, from which solution the

$CoCy_2$ cannot be again precipitated by acids, as it exists now in the form of potassic cobalti-cyanide. $K_6Co'''_2Cy_{12}$.

$$2CoCy_2 + 6KCy + 2HCy = K_6Co'''_2Cy_{12} + H_2.$$

150. "If the solution contains Ni, as well as Co, the addition of HCl to the solution of the cyanides produces a greenish precipitate, which always contains the whole of the Ni, and under particular circumstances all the Co—that is, when these two metals are in the proportion of 3 eq. of Ni to 2 eq. of Co. The precipitate consists then of nickelous cobalticyanide, $Ni_3Co_2Cy_{12}$. In case of a larger proportion of Ni, the precipitate is a mixture of $NiCy_2$ and the former compound; but if the proportion of Ni is smaller, a part of the Co remains in solution as $K_6Co_2Cy_{12}$."—*Will.*

151. Co may be completely precipitated from its neutral solutions by KNO_2 as an orange yellow body (Co_2O_3, $2N_2O_3$, $6(KNO_2)2H_2O$). Before adding the KNO_2 the solution must be evaporated to a small bulk, and neutralised by KHO if it contains excess of acid; acetic acid must be added after the KNO_2 to strongly acid reaction, and the mixture is left to stand for some time. This reaction separates Co from Ni, Mn, Zn, and many other metals.

152. The compounds of Co fused with borax in the loop of a platinum wire, in either flame of the blowpipe, produce a beautiful blue glass, which is a very delicate and characteristic test for Co. The cobalt compound must be used in very small proportion.

153. *Reduction on charcoal splinter.*—"By pulverising the charcoal, white ductile lustrous metallic particles are obtained, which form a brush on the magnetic blade. The metal, rubbed off on to paper, gives a red solution when moistened with HNO_3; this yields a green colour on addition of HCl and drying, which disappears again on moistening. The paper moistened with soda, brought into bromine-vapour and again moistened with soda, yields a brownish-black spot of Co_2O_3. This reaction is plainly seen with a few tenths of a milligramme of metal. The paper can also be used, after washing out the

soda and burning, for the coloration of the borax bead."—*Bunsen.*

Characteristic.—Reactions with KHO, NH_4HO, KCy, KNO_2, and the blow-pipe tests.

154. Co unites with O in several other proportions, the oxide Co_2O_3 is formed as hydrate by suspending CoH_2O_2 in H_2O, and passing into it Cl, $Co_2H_6O_6$ is precipitated as a black powder, whilst $CoCl_2$ remains in solution; thus—

$$3(CoH_2O_2) + Cl_2 = Co_2H_6O_6 + CoCl_2.$$

If the oxide is suspended in solution of KHO it is all converted into $Co_2H_6O_6$. The other oxides of Co are formed by a combination of these two in different proportions. Co_3O_4 is formed by heating CoO to dull redness in the air, or by igniting Co_2O_3. Co_2O_3 is converted into cobaltous salts on being heated with acids.

155. Answers to the following exercises must be written out:

EXERCISES.

44. In what state do Co, Ni, Mn, and Zn, occur in nature?

45. If I desired to precipitate manganese completely from a solution by ammonia, in what state must I take care to have it in the solution?

46. A mixture of MnO, NiO, and CoO, is placed in a tube, a current of dry HCl gas is passed over it, and it is at the same time exposed to a moderate red heat; the transmission of the gas, and the ignition, is continued until the formation of H_2O ceases; what change has the HCl effected? Dry H is then passed over it, and a stronger heat applied until a slight cloud only is perceptible upon approaching a glass rod, moistened with ammonia, to the mouth of the tube—what changes has the H effected?

47. If you had to manufacture zinc sulphate, what substance or substances would you employ; give the composition of the crystallised salt.

48. A mixture of ZnO, NiO, and CoO, is mixed with sugar, and the mixture is then placed in a covered crucible, which is

then heated gradually, until it attains the very highest degree obtainable in a wind furnace, at which temperature it is kept for some time. State what changes the oxides have undergone, and what remains in the crucible?

49. When any of the oxides of manganese are ignited in contact with the air, in what state are they left?

50. A mixture of MnO, NiO, ZnO, and CoO, is placed on a piece of porcelain and inserted in a tube; a stream of dry H_2S is passed through the tube, and the tube is then heated to dull redness; after allowing the substance to cool in the tube in an atmosphere of the H_2S, it is digested for some time in cold dilute HCl,—what occurs? To the filtered HCl solution is added sodic acetate in excess, and H_2S is then passed through the solution. What changes take place, and why is the sodic acetate added?

51. Name the principal ore of manganese, and state for what it is chiefly employed; illustrate your answer by an equation.

52. Illustrate by means of equations the changes which take place in a solution containing a salt of nickel and one of cobalt (say $NiSO_4$ and $CoCl_2$), when a solution of KCy is added in excess, and the solution afterwards slightly acidulated with H_2SO_4:—(1) When the metals are in the proportion of 3 atoms of Ni to 2 of Co; (2) When they are in the proportion of 6 of Ni to 2 of Co; (3) When they are in the proportion of 3 of Ni to 6 of Co.

53. I treat a mixed precipitate of the sulphides of Mn, Ni, Zn, and Co, with acetic acid. What change (if any) takes place?

54. A colourless solution is given you to examine for the members of the first, second, and third groups. State what members of these groups are probably absent.

55. Describe the chief properties and the applications of Ni and Co.

56. Describe the changes which would take place on roasting ZnS at a gentle heat in contact with the air, and exposing the roasted mass to a red heat.

57. Describe as many methods as possible for separating the members of this group by the aid of Table III and the text.

58. How is NH_4HS and $(NH_4)_2S$ prepared, and describe by means of equations the changes which take place on treating neutral solutions of $MnCl_2$ with these sulphides?

59. I mix ZnO, obtained by roasting blende or calamine, with one half its weight of charcoal, coke, or anthracite in powder. The mixture is introduced into a crucible, in the bottom of which is an opening into which an iron pipe has been accurately fitted; the upper end of the tube reaches nearly to the top of the crucible, the lower end projects some distance out of it. After the introduction of the mixture the crucible is covered with a lid, made air-tight by means of fire-clay; the crucible is then placed in a furnace, in the sole of which there is a hole for the lower end of the iron tube to pass through; the crucible is exposed in the furnace to a strong heat—what occurs?

60. How is potassic nitrite prepared?

61. How is chlorine prepared?

62. Describe a method for the preparation of microcosmic salt, and give its formula.

63. Describe by means of equations the two methods given in Part III for the preparation of potassic cyanide.

FOURTH GROUP.

ALUMINIC OXIDE (Al_2O_3), CHROMIC OXIDE (Cr_2O_3), FERRIC OXIDE (Fe_2O_3), FERROUS OXIDE (FeO).

ALUMINIC, CHROMIC AND IRON PHOSPHATES; THE PHOSPHATES OF THE ALKALINE EARTHS. BARIC, STRONTIC, AND CALCIC OXALATES.*

URANIC OXIDE (U_2O_3). TITANIC OXIDE (TiO_2).

Solutions for reactions.—Al_23SO_4, Cr_2Cl_6, Fe_2Cl_6, $FeSO_4$ in H_2O.

156. *Examination for the members of the group.*—When a solution is examined for the members of this group only, the

---

* The phosphates and oxalates do not engage the attention of the student as he passes through the basic groups; he has therefore only to

group reagent, NH_4HO, must be added, as directed at par. 363, and the precipitate, after being thoroughly washed with boiling water, must be examined for the *members of this group* and also for Mn, as it is precipitated in greater or less quantity by NH_4HO; the cause of its precipitation is explained in par. 128. We shall describe three methods for the examination of this group; the first or second is probably the best when Fe or Mn is present. Separate portions of the *original* solution must be tested for Fe both in the ferrous and ferric states; for Fe'' according to par. 177, for Fe''' according to par. 176 or 179, the latter if Cu is in the solution. A small portion of the precipitate must be examined for Mn by the blowpipe test (par. 130).

157. *1st Method.*—Fuse* the precipitate with equal parts of Na_2CO_3 and $NaNO_3$† or KNO_3 in a platinum crucible; after the fusion, allow the mass to cool, and then boil it with water and filter. If much Cr is present the filtrate will have a *yellow colour;* add to the filtrate acetic acid in excess, then $Pb(\bar{A})_2$; if a *yellow* precipitate ($PbCrO_4$) is produced‡ a chromic compound is present in the substance under examination. Dissolve the residue in HNO_3, add NaHO in excess, warm the solution and filter, to the filtrate add HNO_3 in excess, then NH_4HO in excess, and again warm the solution; if no precipitate should appear, even after some time (half an hour), no ALUMINIC COMPOUND *is present.*

deal with the substances given in Table IV. It is not until he has had some practice in examining both for acids and bases that the insoluble salts which are precipitated along with the oxides of this group are included in the course; the precipitate is then examined according to Table V. Manganous phosphate is also precipitated by NH_4HO, although it has not been included in the list of phosphates precipitated by that reagent.

Uranic and titanic oxides are classed amongst the rare substances; they do not therefore form a part of the group, and are therefore not included in Tables IV or V.

* See Fusion, in Part III.

† About one part of the precipitate to two of Na_2CO_3 and two of KNO_3.

‡ The sodic carbonate and nitrate employed in the fusion must be entirely free from sulphate, otherwise, on the addition of $Pb(\bar{A})_2$, a white precipitate of $PbSO_4$ will be formed, which the student might mistake for $PbCrO_4$.

TABLE IV.

BEHAVIOUR OF THE FOURTH GROUP WITH THE SPECIAL REAGENTS.

Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.
L 1. Al_2O_3 and $Al_2H_6O_6$ are *white*.	M 1. Cr_2O_3 is green, and $Cr_2H_6O_6$ a *bluish green powder*.	N 1. F_2O_3 and $Fe_2H_6O_6$ are of a *reddish brown* colour.	O 1. FeO is *black;* FeH_2O_2 is *white*.*
L 2. NH_4HO, *even* in the presence of its salts, precipitates from *aluminic* solutions $Al_2H_6O_6$, which an excess of the reagent *does not* redissolve.	M 2. NH_4HO, *even* in the presence of its salts, precipitates from *chromic* solutions $Cr_2H_6O_6$, which an excess of the reagent *does not* redissolve.	N 2. NH_4HO, *even* in the presence of its salts, precipitates from *ferric* solutions $Fe_2H_6O_6$, which an excess of the reagent *does not* redissolve.	O 2. NH_4HO, *but not* in the presence of its salts, precipitates from *ferrous* solutions FeH_2O_2, which an excess of the reagent *does not* redissolve.
L 3. The *fixed Alkalies* precipitate from *aluminic* solutions $Al_2H_6O_6$, which is *soluble* in an excess of reagent, from which solution it may be again precipitated on the addition of NH_4Cl.	M 3. The *fixed Alkalies* precipitates from *chromic* solutions $Cr_2H_6O_6$, which is *soluble* in an excess of the reagent in the *cold;* but on *boiling* the solution it is again precipitated.	N 3. The *fixed Alkalies* precipitate from *ferric* solutions $Fe_2H_6O_6$, *insoluble* in an excess of the reagent.	O 3. The *fixed Alkalies* precipitate from *ferrous* solutions FeH_2O_2, *insoluble* in an excess of the reagent.
L 4. $(NH_4)_2CO_3$ precipitates from *aluminic* solutions $Al_2H_6O_6$. This precipitation is attended with an evolution of CO_2.	M 4. $(NH_4)_2CO_3$ precipitates from *chromic* solutions $Cr_2H_6O_6$, CO_2 being given off.	N 4. $(NH_4)_2CO_3$ precipitates from *ferric* solutions $Fe_2H_6O_6$, CO_2 being given off.	O 4. $(NH_4)_2CO_3$ precipitates from *ferrous* solutions $FeCO_3$, soluble in NH_4Cl.

---

* The student will most probably not obtain the precipitate of the colours here stated, as ferrous salts are rarely ever free from ferric salts, and the colours of the precipitate by this mixture are altered.

The fixed alkaline carbonates throw down from their solutions all the members of this group, some as oxides, the rest as carbonates. An excess of the reagent does not redissolve the precipitate.

The alkalies fail to precipitate the members of this group in the presence of non-volatile organic matter, such as starch, sugar, tartaric acid, &c.

158. *2nd Method.*—The *group precipitate* after being carefully *washed* and *dried* is dissolved in strong HNO_3 and boiled, fragments of $KClO_3$ being added from time to time till the oxidation is complete, which generally happens in four or five minutes if no water is present, as H_2O retards the oxidation; KHO is then added in excess, $Fe_2H_6O_6$ and $Mn_2H_6O_6$ will be precipitated if present; filter if necessary and add to the filtrate NH_4Cl and NH_4HO, which will precipitate $Al_2H_6O_6$ if present; filter if necessary and add to the filtrate $BaCl_2$ or $Ba(NO_3)_2$, a yellow precipitate of $BaCrO_4$ will be produced if chromic oxide were present.—(*Barth.*)

159. *3rd method.*—Dissolve the precipitate in as small a quantity of boiling dilute HCl as possible; add to this acid solution when cold, a cold solution of NaHO or KHO, which will precipitate $Fe_2H_6O_6$(N3) *if* Fe is *present*;* filter when a precipitate is produced and boil the *filtrate*, or the *solution* in which there was no precipitate, in a dish for a considerable time; if a precipitate is produced by the boiling it is due to Cr_2O_3; filter, and add to the filtrate, or to the solution which has failed to give a precipitate, HCl, until the solution is acid, then add *one grain* of $KClO_4$, and warm the solution so as to destroy all organic matter; add, lastly, NH_4HO in excess, and again warm the solution; if no precipitate should appear, allow it to stand for a short time (half an hour); if no precipitate should even then appear Al_2O_3 *is absent.*

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, AND THE SULPHATES OF THE GROUP.

160. *The metals.*—Cr and Al are not oxidized when heated even to redness in the open air. Fe oxidizes at the common temperatures in moist air. Al and Fe oxidize, Al only slowly,

---

* Manganese, if present, will also be precipitated by the sodic or potassic solution, so that a precipitate may be produced by the alkali when ferric oxide is absent.

in an atmosphere of steam at a red heat, Al_2O_3 and Fe_3O_4 being formed. Fe decomposes also at a red heat CO_2 and CO. Cr is not acted upon by any acid except HF.* Al is not acted upon in the cold by strong or dilute HNO_3, and very slowly at the boiling heat; dilute H_2SO_4 dissolves it with difficulty, but HCl, either dilute or concentrated, dissolves it readily even at low temperatures, Al_2Cl_6 being formed. Pure Fe is scarcely acted upon by acids at the ordinary temperature, but dissolves with the aid of heat, H being evolved; but Fe as usually obtained dissolves readily in dilute mineral acids, but strong HNO_3 covers it with a film of Fe_2O_3, which prevents the further action of the acid, whether dilute or undilute; but reducing agents remove the film, the *passive* iron is thereby again rendered active and capable of dissolving in dilute HNO_3. Al is not acted on by H_2S or by $(NH_4)_2S$; KHO or NaHO in a state of fusion do not act upon it, but their solutions dissolve it readily, forming $Al_2Na_6O_6$ or $Al_2K_6O_6$ and H being evolved. Cr and Fe are oxidized by fusion with KNO_3, K_2CrO_4 and K_2FeO_4 being formed. Al may be obtained by passing Al_2Cl_6 in vapour over Na, and Cr may be obtained by passing the vapour of Cr_2Cl_6 over Zn.

161. *The Oxides.*—Al_2O_3, Cr_2O_3 and Fe_2O_3 may be obtained by igniting their hydrates; FeO by precipitating FeH_2O_2 from a ferrous salt by an alkali, and boiling it in a vessel from which O is excluded, the hydrate being rendered anhydrous below the boiling point. They are not altered by heat except Fe_2O_3, which, at a white heat, is converted into Fe_3O_4, and FeO is converted, on exposure to air without the aid of heat, into

---

* The properties of Cr differ considerably according to the manner in which it is prepared, the difference depending doubtless on the state of aggregation. Cr made by Peligot's process oxidizes with great facility, taking fire in the air even at a heat below redness; it also dissolves in dilute H_2SO_4 and HCl, and is oxidized by HNO_3. The properties of most metals vary very much with the state of aggregation; thus, even lead and several other metals, which will only combine with the oxygen of the air with vivid combustion at very high temparatures when in masses, will when in a state of fine powder, combine with the oxygen of the air with vivid combustion at the ordinary temperature of the atmosphere.

Fe_2O_3. Al_2O_3 and Cr_2O_3 are not reduced by H, Al_2O_3 is not reduced by C, and Cr_2O_3 is reduced by C at a white heat, but only at the points of contact; the oxides of Fe are reduced by H and C with the aid of heat. Al_2O_3 and Cr_2O_3 are unaltered on being heated with S, but FeO and Fe_2O_3 are converted by it into FeS with evolution of SO_2. Al_2O_3 and Cr_2O_3 are not converted into chlorides by Cl unless they are mixed with C (see note, page 30); Cl displaces the O in the iron oxides. FeO and Cr_2O_3 are, with one other oxide (the molybdic), the only oxides which melt at a temperature below that of the metal from which they are produced. *The hydrates* may be obtained by adding to a solution of their salts NH_4HO, or one of the fixed alkalies, or in the case of $Al_2H_6O_6$, $Cr_2H_6O_6$, and $Fe_2H_6O_6$ by adding $(NH_4)_2CO_3$, as shown in Table IV. $Al_2H_6O_6$ and $Cr_2H_6O_6$ may also be obtained by adding $(NH_4)_2S$ to a solution of their salts with evolution of H_2S, thus;

$$Al_2(SO_4)_3 + ((NH_4)_2S)_3 + 6H_2O = Al_2H_6O_6 + ((NH_4)_2SO_4)_3 + 3H_2S.$$

FeO is the only member which is acted upon by Cl when suspended in pure H_2O, or in a solution moderately alkaline. The following is the change in H_2O:

$$3FeO + Cl_2 = Fe_2O_3 + FeCl_2.$$

If it be suspended in an alkaline liquid the following is the reaction:

$$2FeO + 2KHO + Cl_2 = Fe_2O_3 + 2KCl + H_2O.$$

Fe_2O_3 may be converted into a higher oxide (ferric acid) by Cl if the solution contains a large quantity of KHO, thus:

$$Fe_2O_3 + 10KHO + 3Cl_2 = 2(K_2FeO_4) + 6KCl + 5H_2O$$

These oxides and their hydrates are insoluble in H_2O, but they dissolve in the dilute mineral acids; after ignition, however, they dissolve with great difficulty, even in the concentrated mineral acids; but even after ignition, if fused with $KHSO_4$, they dissolve readily along with the other fused particles in H_2O. Although it has just been stated that these oxides and their hydrates are insoluble in H_2O, a modification of aluminic hydrate, which will be noticed under the remarks on Aluminic Compounds (par. 167), is soluble in H_2O, and it appears probable there is also a soluble ferric hydrate.

162. *The Sulphides.*—It has already been stated that aluminic and chromic sulphides are not formed in the humid way, but they may be obtained by passing the vapour of CS_2 over the Al_2O_3 and Cr_2O_3 intensely heated. These sulphides are black, they are decomposed by H_2O into hydric oxides, H_2S being evolved. Fe_2S_3 and FeS may be obtained in the anhydrous state by the direct combination of Fe and S; the colour of the first is yellowish-grey and the other yellow. Fe_2S_3 may be obtained in the hydrated state by dropping a solution of a ferric salt into a solution of an alkaline sulphide which is in excess, or by passing H_2S over the dry hydrate; this sulphide is speedily altered by exposure to air, Fe_2O_3 being formed and S set free;* if the alkaline sulphide is added to the solution of the ferric salt, ferrous sulphide is formed and S set free; thus—

$$(Fe_23SO_4)_2 + ((NH_4)_2S)_6 = 4FeS + S_2 + ((NH_4)_2SO_4)_6.$$

Alkaline sulphides precipitate from solutions of ferrous salts FeS in the hydrated state; its colour is black; it is insoluble in alkalies and alkaline sulphides, but dissolves readily in HCl and HNO_3; it oxidizes quickly on exposure to air, turning reddish brown, Fe_2O_3 being formed and S set free.

163. *The chlorides.*—Al_2Cl_6, Cr_2Cl_6 and Fe_2Cl_6 may be obtained in the hydrated state by dissolving the anhydrous

---

* Ferric hydrate is employed to some extent in removing H_2S from coal-gas; for this purpose it is mixed with saw-dust and placed in layers about twelve inches deep on perforated shelves; when the mixture ceases to remove the H_2S, ferric oxide is reproduced and S set free by exposing the Fe_2S_3 to a current air; the revivified oxide is again employed, and this continues until the accumulation of S in the mixture impairs its absorbing power; the S is then utilised by the sulphuric acid manufacturer, and the Fe_2O_3 which remains may be again employed for purifying the gas.

chlorides in water or the sesquioxides of these metals in HCl; these hydrous chlorides cannot be rendered anhydrous by heating them in the air, as they are decomposed into the corresponding metallic oxides, HCl being evolved. Al_2Cl_6, Cr_2Cl_6, and Fe_2Cl_6 may be obtained in the anhydrous state; the first two by heating a mixture of Al_2O_3 or Cr_2O_3 with C and igniting in a current of dry Cl; the following is the reaction:—

$$Al_2O_3 + 3C + 3Cl_2 = Al_2Cl_6 + 3CO.$$

Fe_2Cl_6 may be obtained by passing dry Cl over Fe heated to redness; these anhydrous chlorides are volatile, deliquescent, and dissolve readily in H_2O with considerable evolution of heat; Fe_2Cl_6 is reduced by H_2S and other reducing agents to the state of ferrous chloride. Anhydrous $FeCl_2$ may be prepared by passing dry HCl gas over ignited Fe; it may be obtained in the hydrated state by dissolving Fe in HCl; it is very soluble in H_2O and if heated in the open air Cl escapes and Fe_2O_3 remains; it is converted into Fe_2Cl_6 on passing Cl into its solution. Al_2Cl_6 is not decomposed at any temperature by H; if H be passed over perfectly anhydrous Cr_2Cl_6, very gently heated, $CrCl_2$ is formed; if the heat be strong, Cr is separated; the iron chlorides are decomposed by H with the aid of heat, HCl being formed and Fe remaining.

164. *The nitrates* may be obtained by dissolving the oxides in HNO_3; they are soluble in H_2O, and readily decomposed by heat.

165. *The sulphates*, $Al_2(SO_4)_3$, $Cr_2(SO_4)_3$, and $Fe_2(SO_4)_3$ may be obtained by dissolving the hydrates of these metals in H_2SO_4; the first is also formed by adding to clay which has been gently heated H_2SO_4 and then heating the mixture for a considerable time; the latter may be prepared by adding to every 1 eq. of $FeSO_4$ in solution $\frac{1}{2}$ eq. of H_2SO_4, and then adding to the heated liquid HNO_3 in small quantities as long as any red fumes are given off. These sulphates are soluble in H_2O; they are decomposed by heat, the metallic oxides being

left; they and $Mn'''_2(SO_4)_3$ form with the alkaline sulphates double salts, which are termed alums. The general formula for this class of salts is $M'''_2(SO_4)_3$, $M_2SO_4 + 24H_2O$. A solution of $Fe_2(SO_4)_3$, especially if it contains a little free acid, dissolves many metals, even Ag, and the $Fe_2(SO_4)_3$ is reduced to $FeSO_4$. $FeSO_4$ may be obtained by dissolving Fe in H_2SO_4; it is also formed by the conversion of iron pyrites (FeS_2) into FeS, and this by oxidation into $FeSO_4$. It crystallizes with seven atoms of H_2O; the crystals, when pure, are bluish green, but if they contain ferric sulphate they are grass green; at a red heat $FeSO_4$ is decomposed into Fe_2O_3, SO_2, and SO_3; the little water which distils over forms with the SO_3 the Nordhausen sulphuric acid.*

166. *The general characters of the salts of this group.*—Aluminic salts, with the exception of the chloride, are colourless, both in the hydrous and anhydrous states. Chromic oxide forms at least two varieties of salts; there is a variety which is uncrystallizable and of a *green* colour, another variety is crystallizable and of a *violet* colour; the solutions of the violet salts change to green on heating, and the green solutions generally transmit a red light. Ferric salts are nearly *white* in the anhydrous, and *yellow* or *yellowish red* in the hydrous state; the colour of the solutions is *brownish yellow.* Ferrous salts are *white* in the anhydrous and *bluish green* in the hydrous state; their solutions, if concentrated, have a *greenish* colour. Ferric salts are converted into ferrous ones by reducing agents, as nascent H, H_2S, SO_2, Fe, Zn, $SnCl_2$, &c. Ferrous salts are converted into ferric ones by oxidizing agents, as O, Cl, HNO_3, &c. Solutions of the ferrous salts rapidly absorb O from the air, and if the solution is neutral a yellow basic ferric salt is deposited. The soluble neutral salts of the metals of this group *redden* litmus paper, and are decomposed by heat. The members of this group are precipitated by

---

* This acid has a composition corresponding to H_2SO_4, SO_3 it is principally prepared at the town of Nordhausen, in Saxony, by drying crystallized ferrous sulphate at a moderate heat to expel the water of crystallization, and then distilling the dried sulphate in earthen retorts.

$(NH_4)_2S$, Al and Cr, as hydric oxides, consequently H_2S is always evolved when $(NH_4)_2S$ is added to a solution containing either or both these metals. FeS is always formed when $(NH_4)_2S$ is added either to a solution of ferrous or ferric salts. Fe_2O_3, and also Al_2O_3, are frequently separated from their solutions, and from other bases, by adding an alkaline acetate or formiate, previously adding to the solution one of Na_2CO_3 or $(NH_4)_2CO_3$ until the precipitate which is formed *only just* redissolves on stirring; the formiate or acetate is then added, and the solution boiled; ferric and aluminic acetates or formiates are formed in the first instance, and are decomposed by boiling into *insoluble* basic acetates or formiates. Fe_2O_3 and Al_2O_3 are completely precipitated from solutions of their salts *in the cold* by digesting in the solutions finely powdered $BaCO_3$ or $CaCO_3$; they are precipitated principally in the state of hydrates and partly as basic salts. Other insoluble carbonates also precipitate them; thus, if it is desired to purify $MnCl_2$ or $ZnSO_4$ from a ferric salt, it may be accomplished by boiling the solution of the $MnCl_2$ with $MnCO_3$, and the solution of the $ZnSO_4$ with $ZnCO_3$. Cr_2O_3 is also precipitated from its solutions by digesting with $BaCO_3$, but the precipitation takes place *in the cold* only after long-continued digesting. $BaCO_3$ does not precipitate FeO from solutions of ferrous salts, with the exception of the sulphate, when it is digested in the solutions in the cold. The members of this group, with the exception of FeO, differ from the preceding group by being insoluble in NH_4HO, and they and the third group differ from those of the fifth and sixth by not being precipitated by H_2S in the presence of *free* mineral acids.

REMARKS ON THE INDIVIDUAL MEMBERS OF THIS GROUP, WITH ADDITIONAL SPECIAL TESTS.

167. Al *and its compounds.*—Al is a bluish-white metal, very malleable, ductile, and sonorous; it is very light, its sp.

gr. being about 2·5; its sp. heat is very great, its melting-point is intermediate between the melting-points of Zn and Ag, but nearer to the former; it is a better conductor of heat than Ag, and about equal to it as a conductor of electricity. The now well-known alloy of aluminum and copper, viz. *aluminum bronze*, contains 10 per cent. of Al. In combination it is very abundant in nature; it forms not only the basis of common clay, but is likewise a principal ingredient in many of the precious stones. As Al_2O_3, with slight traces of SiO_2 and Fe_2O_3, it forms the CORUNDUM, SAPPHIRE, RUBY, DIAMANT SPAR, &c. As hydrate, it is known under the names DIASPORE and GIBBSITE. Combined with silica and glucina, it forms the EMERALD, BERYL, EUCLASE, and CHRYSOBERYL. Al_2O_3 has the property of combining very intimately with certain kinds of organic matter, especially colouring matters; it attaches itself to the fibres of cloth, and retains in the cloth the power of attracting and retaining colouring matters; its salts are therefore extensively employed as mordants. It is obtained in a form soluble in H_2O by exposing a dilute solution of an aluminic acetate to a temperature of 100° C. in a close vessel for several days; this solution is coagulated by mineral and most vegetable acids, by alkalies and decoctions of dye woods, but the alumina in this form does not act as a mordant. Al_2O_3 is the only oxide known of Al; it is regarded as a sesquioxide on account of its isomorphism with, and general resemblance in properties to, Fe_2O_3.

168. If aluminic compounds be ignited upon charcoal by the blowpipe flame, afterwards moistened with a few drops of $Co(NO_3)_2$, and again strongly heated, the mass assumes a BLUE COLOUR on cooling. This can only be used as a confirmatory test, as other substances, phosphates and readily fusible salts, exhibit the same reaction.

Characteristic.—The reactions with NH_4HO, KHO, and the blowpipe test.

169. Cr *and its compounds.* — The principal mineral of Cr, and from which the oxide is obtained, is the CHROME IRON (FeO, Cr_2O_3), which is found principally in Sweden, in the

Uralian Mountains, and in America; it is scarcely attacked by any of the acids.

170. On fusing any chromic compound, with KNO_3, or $NaNO_3$, yellow *chromate* of the alkali (M_2CrO_4) is formed, which is soluble in water, and by adding to the solution acetic acid in excess, and then $Pb\bar{A}_2$, yellow $PbCrO_4$ precipitates; this test distinguishes it from all other substances. In the fixed alkalies, a small quantity of Cr_2O_3 in the presence of a large quantity of Fe_2O_3 is totally insoluble; but a small quantity of the latter dissolves readily when a large quantity of the former is present. Under these circumstances the two oxides are best separated from each other by fusing the mixed substances with KNO_3 and Na_2CO_3. On treating the fused mass with water, the K_2CrO_4 dissolves, but the Fe_2O_3 does not. The solution may be tested with $Pb\bar{A}_2$.

171. If a solution of Cr_2O_3 in NaHO or KHO is boiled with PbO_2 in excess for a short time, the Cr_2O_3 reduces some of the PbO_2, $PbCrO_4$ being formed, which dissolves in the alkaline solution; if to the filtered liquid acetic acid be added in excess, the $PbCrO_4$ precipitates.

172. *Borax* dissolves chromic compounds, both in the inner and outer blowpipe flame; the bead, on cooling, assumes an EMERALD GREEN COLOUR. *Microcosmic salt* has the same effect.

Characteristic.—The colour of its salts, its conversion by oxidizing agents into chromic acid, and the blowpipe test.

173. Three other oxides of Cr are known, viz. CrO, a base; CrO, Cr_2O_3, corresponding to magnetic oxide of iron; and CrO_3, an anhydride, which forms salts with bases, and is noticed amongst the acids. CrO is known only in the hydrated state; it is obtained by adding KHO to a solution of $CrCl_2$; it absorbs O with great rapidity; it decomposes even H_2O, H being evolved, and the other oxide (CrO, Cr_2O_3, H_2O) in the hydrated state being formed. Chromic oxide and many of the chromates are employed as colouring materials in painting on porcelain and in calico printing.

174. Fe *and its compounds.*—Very little is known about perfectly pure Fe; it is met with in the arts in three different forms, *cast iron*, *malleable iron*, and *steel*; each of these varieties contains carbon and other foreign matters, but the differences of character in these varieties appear to be chiefly due to the different proportions of C which are disseminated through, or combined with, the metal. The ores of iron are numerous, the most valuable are *specular* iron ore, red hæmatite, varieties of Fe_2O_3, brown hæmatite ($2Fe_2O_3$, $3H_2O$), spathic iron or carbonate of iron ($FeCO_3$), clay ironstone and the black band are an impure ferrous carbonate, and the magnetic iron ore, or loadstone (FeO, Fe_2O_3).

175. *Potassic ferrocyanide* (K_4FeCy_6) produces, in *ferrous* solutions, a white precipitate of FeK_2FeCy_6, which speedily becomes *blue* by absorbing oxygen from the air. Free alkalies prevent its formation, and they readily decompose it. It is insoluble in the dilute acids.

176. K_4FeCy_6 produces, even in highly dilute *ferric* solutions, a beautiful blue precipitate of Prussian blue, $Fe_4(FeCy_6)_3$, which is insoluble in acids, but is decomposed by the alkalies; in highly dilute solutions only a blue tinge is produced at first; after long standing a scanty precipitate is formed. The same precautions are required in this case as in par. 177.

177. *Potassic ferricyanide* ($K_6Fe_2Cy_{12}$) produces in *ferrous* solutions a beautiful blue-coloured precipitate of TURNBULL'S BLUE ($Fe_3Fe_2Cy_{12}$), which is insoluble in HCl, but is decomposed by the alkalies. In highly dilute solutions only a bluish-green coloration is produced. If the solution is alkaline, it must be acidified with acetic acid; if it is acid, and the acidity is caused by one of the mineral acids, as they decompose both the potassic ferri- and ferro-cyanides, rendering their solutions green, an alkaline acetate must be added in sufficient quantity so that the base of the acetate may neutralize the free mineral acid.

178. $K_6F_2Cy_{12}$ deepens the colour of the solution of ferric salts to a ruddy brown, but causes no precipitate; if the ferri-

cyanide contains a trace of ferrocyanide,* it will impart to the ferric solution a greenish tinge.

179. Potassic sulphocyanide (KCyS) produces in neutral and even in moderately acid, ferric solutions a very intense blood red, arising from the formation of $Fe_2(CyS)_6$, which is soluble. The colour disappears on the addition of an alkaline acetate, but is restored by adding to the solution dilute HCl; it also disappears on the addition of alkalies, or of a large quantity of strong acid. This is by far the most delicate test for ferric compounds.

180. *Flame reactions.—Reduction on charcoal splinter* gives no metallic bead or ductile lustrous particles; the finely divided metal forms a black brush on the end of the magnetized knife-blade; this, when rubbed off on paper and dissolved in a drop of aqua regia, yields a yellow spot when warmed over the flame, which, when moistened with K_4FeCy_6, gives a deep coloration of *Prussian blue.* The yellow spot moistened with NaHO, and then held for a few moments in a vessel with bromine vapour, gives, on a second addition of soda, no coloration of a higher oxide.

181. *Borax bead.*—"In the oxidizing flame, when hot, yellow to brownish red; when cold, yellow to brownish yellow; reducing flame, bottle green."—*Bunsen.*

Characteristic.—For ferrous compounds, the reactions with $K_6Fe_2Cy_{12}$; for ferric compounds, the reactions with K_4FeCy_6 and KCyS.

182. Two other iron oxides are known, viz. the black or magnetic oxide, Fe_3O_4, which may be viewed as a compound of FeO and Fe_2O_3, and ferric acid. The magnetic oxide occurs in nature; it may be formed, as we have already noticed, by passing steam over Fe, and it may be obtained in the hydrated state by dissolving a ferrous and ferric salt in equal atomic proportions, and adding to the solution KHO or NaHO. Ferric acid, H_2FeO_4, may be obtained, we have seen, by fusing Fe

---

* The solution of potassic ferricyanide ought to be made as it is wanted as it decomposes when in a state of solution, a trace of ferrocyanide being formed.

with KNO_3 (160), or by passing Cl into an alkaline solution of Fe_2O_3 (161).

Answers to the following exercises must be written out.

EXERCISES.

64. Name the substances which will be precipitated when $(NH_4)_2S$ is added to an aqueous solution containing Al_23SO_4, Cr_2Cl_6, Fe_2Cl_6, $FeSO_4$, $ZnSO_4$, $Co(NO_3)_2$, and K_2SO_4, and the form in which they will be precipitated.

65. A solution which has to be examined for the members of this and the preceding groups is alkaline to test-paper; the alkalinity is found to be due to the presence of Na_2CO_3: what members must be absent?

66. I have a quantity of zincic sulphate which contains some ferrous sulphate: how must I get rid of the iron so that after its removal no other salt but the zinc sulphate will remain in solution?

67. How are ferrous and ferric oxides distinguished from each other? Illustrate your answer by equations.

68. The members of the third and fourth groups have been precipitated together by $(NH_4)_2S$: how must the precipitate be treated so as to isolate and detect each of the members (the phosphates and oxalates not being present)?

69. How are potassic ferrocyanide and ferricyanide prepared?

70. I require some ferric chloride, and I have only some ferrous sulphate: how must I proceed so as to obtain from the latter salt the Fe_2Cl_6?

71. How can the precipitation of $Fe_2H_6O_6$, $Al_2H_6O_6$, and of $Cr_2H_6O_6$, from solutions of their salts by the alkalies, be prevented?

72. Ferric oxide is employed to purify coal gas; on ceasing to purify it, it is exposed to the air; the exposure restores its purifying powers. State what impurities it removes, and how

the air revivifies it; state what impurity calcic hydrate removes which the iron oxide does not remove.

73. You are given a solution which is neutral to test-paper, and which can contain only the members of this and the preceding groups: what members must be absent, and what salts of those members *which may be present* must be absent either from their insolubility or from their being alkaline or acid to test-paper? (The student is only expected to answer it to the extent of the salts with which he has been made acquainted in the first four groups.)

74. I fuse in a furnace 2 parts of chrome iron mixed with 1 part of potassic nitrate; I treat the fused mass with water, and add H_2SO_4 or HNO_3 until the solution is acid to test-paper; I then evaporate the solution to the crystallizing point, and allow time for the crystallization. State what substances are formed in the fusion, what substances are dissolved and what are not dissolved by the water, what alteration the added acid effects, and what substance crystallizes out.

75. There is present in a solution Fe_2Cl_6, Al_2Cl_6, $CoCl_2$, $MnCl_2$ and $NiCl_2$; the solution is placed in a flask, $BaCO_3$ is added a little in excess, the flask is corked and allowed to stand some time in the cold, with occasional shaking. What occurs? The mixture is filtered into a flask, the filtrate is slightly acidulated with HCl, Cl is then transmitted through it to saturation, $BaCO_3$ or $CaCO_3$ is then added slightly in excess, the mixture is allowed to stand some hours in the cold and shaking it repeatedly. State the changes which ensue.

76. How is ammonic sulpho-cyanide prepared?

77. I wish to prepare some pure $MnCl_2$ from the waste product obtained in the manufacture of Cl by acting on MnO_2 with HCl; it contains, in addition to the $MnCl_2$, Fe_2Cl_3 and HCl. How shall I proceed? I have another quantity of the waste product, containing in addition to the impurities already named some $CuCl_2$, $CoCl_2$, and $NiCl_2$: how shall I proceed in this case to obtain pure $MnCl_2$? Describe a different method in each case.

78. A colourless solution is given you to examine for the members of this and the preceding groups; what members are probably absent?

79. Enumerate the chief ores of iron, and give their composition.

80. There is present in an acetic acid solution Al''', Fe''', Co'', Zn,'' Ni'', and Mn''; H_2S is passed through it; what changes, if any, take place?

81. You have to examine a mixture which can only contain ferrous, ferric, calcic, magnesic, potassic, and ammonic salts: describe the methods you would adopt in the examination.

82. Describe the manufacture of aluminum.

83. Give the composition of Nordhausen sulphuric acid, and state how it is prepared.

84. How would you prepare anhydrous Fe_2Cl_6 and anhydrous Al_2Cl_6?

85. How would you prepare Fe_2S_3?

86. Describe a method for the preparation of PbO_2.

The following SALTS, *being insoluble in Neutral and Alkaline Solutions, are precipitated along with the members of the Fourth Group.**

ALUMINIC, CHROMIC, AND FERRIC PHOSPHATES; THE PHOSPHATES OF THE ALKALINE EARTHS; BARIC, STRONTIC, AND CALCIC OXALATES.

183. Aluminic phosphate varies considerably in composition, according to the proportions of the acting solutions and the temperature at which they are mixed; it behaves in the same way with reagents as Al_2O_3, with this exception, that it is insoluble in acetic acid, whilst Al_2O_3 is soluble. The presence of PO_4, when combined with Al_2O_3, may be detected by the following method:—After having *dissolved* the aluminic compound in a small quantity of HCl, $H_2\overline{T}$ must be added and

---

* The student will do well to omit this section of the group until he has had some practice in detecting the more simple combinations of acid and base.

then NH_4HO in *excess*. If on the addition of $MgSO_4$ to this solution a precipitate be formed, PO_4 is present. When the quantity of acid present is small, the precipitate will not appear until after the lapse of some time; in all cases the formation of the precipitate is much promoted by agitation.

184. PO_4 in combination with Al_2O_3 may also be detected in the following way:—"Add Na_2CO_3 to the HCl solution until the free acid is nearly neutralized; mix with $BaCO_3$ in excess, add solution of NaHO or KHO, and boil. This process gives the Al_2O_3 in solution, the PO_4 in a precipitate of baric phosphate. Dissolve this precipitate in HCl, decompose by H_2SO_4, filter, and test the filtrate with $MgSO_4$, with addition of NH_4Cl and NH_4HO."—*Fresenius*.

185. PO_4 may be detected in almost all salts and most minerals containing it by the ammonic molybdate test (see par. 428).

186. CHROMIC PHOSPHATE behaves in the same way with reagents as Cr_2O_3, with this exception, that it is insoluble in acetic acid, in which reagent the latter is soluble. The presence of PO_4, when combined with Cr_2O_3, may be detected in the same way as when combined with alumina. To ascertain whether Cr_2O_3 and the chromic phosphate are both present in the precipitate produced by boiling the fixed alkaline solution, dissolve the precipitate produced on boiling in HCl, add an *alkaline acetate* in excess; if a precipitate is produced, the PHOSPHATE is present, filter off, and to the filtrate add NH_4HO in excess; if a precipitate is produced, the OXIDE is present.

187. Ferric phosphate, like aluminic phosphate, varies considerably in composition, and from the same causes; it behaves in the same way with reagents as Fe_2O_3, with this exception, that it is insoluble in acetic acid, in which reagent the latter is soluble. $(NH_4)_2S$ decomposes IRON PHOSPHATE,* precipitating the metal in the state of sulphide whilst the acid remains in solution in combination with the ammonia. The acid is therefore sought for in the filtrate, and not in the precipitate, when

---

* Aluminic and chromic phosphates are not decomposed by $(NH_4)_2S$; they are precipitated unchanged by that reagent.

$(NH_4)_2S$ has been employed as the precipitating reagent. The same method may be employed for the detection of PO_4, when combined with Fe, as is employed when this acid is in combination with Al.

188. The different calcic ortho-phosphates are soluble in acetic acid. They may be decomposed in several ways. The following are those which are most applicable in qualitative analysis:—1. Dissolve the phosphate in a small quantity of HCl; add to the solution an alkaline *acetate*, and after that a few drops of Fe_2Cl_3 (*consult* par. 427). FERRIC PHOSPHATE will be precipitated, whilst the Ca will remain in solution along with the excess of the Fe_2Cl_3. To detect the Ca, precipitate Fe by $(NH_4)_2S$, and add to the filtrate $H_2\bar{O}$. If a precipitate be produced, Ca is present. 2. Dissolve the phosphate in a small quantity of HNO_3; add to this solution $HgNO_3$, and then NH_4HO slightly in excess; MERCUROUS PHOSPHATE along with the excess of Hg_2O will be precipitated, whilst the Ca will remain in solution, from which solution it will be thrown down on the addition of $H_2\bar{O}$. Boil the mixed precipitate of mercurous phosphate and oxide in $(NH_4)_2S$; filter, and to the filtrate add NH_4Cl and $MgSO_4$; if a precipitate be produced, it proves the presence of PO_4. The above remarks upon CALCIC PHOSPHATES apply to the corresponding BARIC, STRONTIC, and MAGNESIC salts.

189. CALCIC OXALATE is insoluble in acetic acid. By ignition, this salt, like all the other oxalates, is decomposed, a carbonate being left. To separate the $\bar{O}$ from the Ca, to its *solution* in HNO_3 add $HgNO_3$; $Hg_2\bar{O}$ will be precipitated, whilst $Ca(NO_3)_2$ will remain in solution along with the excess of $HgNO_3$. To detect Ca, remove the Hg from the solution by NH_4HO, and add to the filtrate $H_2\bar{O}$. $Hg_2\bar{O}$ is decomposed by boiling it in $(NH_4)_2S$, Hg_2S being precipitated, whilst the acid remains in combination with ammonia, in which solution it may be detected on the addition of any soluble *calcic salt*. The above remarks apply to the corresponding BARIC and STRONTIC salts.

190. *The following precautions are to be attended to in the*

analysis of this section :—Before dissolving the precipitate produced by NH_4HO, it must be completely freed by washing from all trace of that reagent. Frequently a small precipitate will appear after boiling the NaHO solution, when Cr is absent; the presence of this member must therefore in all cases be confirmed by other tests. Al_2O_3 and its phosphate are sometimes overlooked by the operator, from his neglecting to add acetic acid in excess. The precipitate produced by NaHO, after being well washed, should be dissolved in as small a quantity of HNO_3 as possible, to which solution a moderate quantity of $H_2\overline{T}$ should be afterwards added, and finally NH_4HO in excess; the solution ought, after the addition of these reagents, to be well agitated, and time allowed for the separation of the precipitate. In testing for PO_4 in the ammonic solution, a precipitate will frequently be formed on the addition of $MgSO_4$ when PO_4 is absent. To distinguish the phosphate precipitate from this, the precipitate produced ought to be dissolved in $H_2\overline{T}$, and NH_4HO added in excess. If a precipitate again appears, after agitating the liquid and allowing it to stand, it must be due to the presence of PO_4. The precipitate produced by NH_4HO in the $H_2\overline{T}$ solution must be well washed before dissolving it in dilute HNO_3. A slight turbidness will generally be formed on the addition of $HgNO_3$ to the HNO_3 solution, even in the absence of oxalates, owing to the HNO_3 containing a slight trace of HCl.

191. The following is another method for the separation of the members of the fourth group and the phosphates and oxalates which are precipitated along with them by the group reagent; the precipitate produced by NH_4HO, after being well washed, is ignited upon a piece of platinum foil, or in a small crucible; if one or more of the three oxalates (baric, strontic, and calcic) are present, they will be converted by the ignition into *carbonates;* dissolve the ignited precipitate in as small a quantity of boiling dilute HCl as possible; if it dissolves with *effervescence,* one or more of the three oxalates are present; examine the solution in this case according to par. 192. If the solution is unattended with effervescence, the three oxa-

TABLE V.—PRECIPITATE PRODUCED BY NH_4HO IN THE H_2S FILTRATE.

Dissolve in boiling dilute HNO_3.—*Add an excess of* $NaHO$ *in the cold.*

<table>
<tr>
<td colspan="3">FILTRATE
Chromic Oxide, Chromic Phosphate, Aluminic Oxide, Aluminic Phosphate.
Boil for some time.</td>
<td colspan="5">PRECIPITATE
Ferric Oxide, Ferric Phosphate, and, when in combination with $\overline{O}$ or PO_4, Ba, Sr, Ca; also Mg when in combination with PO_4.
Dissolve in boiling dilute HNO_3, then add $H_2\overline{T}$, and finally NH_4HO in excess.</td>
</tr>
<tr>
<td colspan="2">FILTRATE
Aluminic Oxide and Phosphate.
Add $H\overline{A}$ in excess.</td>
<td rowspan="4">PRECIPITATE
of
Chromic Oxide
and
Phosphate.
Examine for the oxide and phosphate in the way stated in par. 186.</td>
<td colspan="2">FILTRATE
Ferric Nitrate, Ferric Phosphate.
Divide the solution into two parts.</td>
<td colspan="3">PRECIPITATE
The Phosphates and Oxalates of the Alkaline Earths.
Dissolve in HNO_3, and add solution of $HgNO_3$.</td>
</tr>
<tr>
<td>FILTRATE
Aluminic Oxide.
Add
Na_2HPO_4.</td>
<td rowspan="3">PRECIPITATE
Aluminic Phosphate.</td>
<td>To one part add $H\overline{A}$ until the solution possesses an acid reaction; then add K_4FeCy_6.</td>
<td>If Fe has been found, add to the other part NH_4Cl and $MgSO_4$.</td>
<td colspan="2">FILTRATE
Ba, Sr, or Ca, originally in combination with $\overline{O}$, and the Phosphates of the Alkaline Earths, along with the excess of $HgNO_3$.
Add NH_4HO slightly in excess.</td>
<td rowspan="2">PRECIPITATE
Mercurous Oxalate.
Confirm the presence of $\overline{O}$ by boiling the precipitate in $(NH_4)_2S$; filter, and acidify with $H\overline{A}$; filter, if necessary, and then add to the solution $CaSO_4$.</td>
</tr>
<tr>
<td rowspan="2">PRECIPITATE
Al as a phosphate.</td>
<td>If a blue precipitate is formed it shows the presence of Fe.</td>
<td>If a precipitate is formed after agitating the fluid and allowing it to stand for some time, it shows the presence of PO_4.</td>
<td rowspan="2">FILTRATE
$Ba(NO_3)_2$,
$Sr(NO_3)_2$,
$Ca(NO_3)_2$,
and
$Mg(NO_3)_2$.
Examine the filtrate for the alkaline earths in the usual way.</td>
<td>PRECIPITATE
Mercurous Phosphate
Along with the excess of Hg_2O. Boil the precipitate in $(NH_4)_2S$; filter, and to the filtrate add NH_4Cl and $MgSO_4$.</td>
</tr>
<tr>
<td colspan="2">Note.—To ascertain whether there was any Fe uncombined with PO_4, add to the original solution $Na\overline{A}$; filter, and to the filtrate add K_4FeCy_6.
If a blue precipitate is formed, it proves that all the Fe did not exist as phosphate.</td>
<td>If a precipitate is formed after agitating the liquid and allowing it to stand for some time, it proves the presence of PO_4.</td>
<td>If a precipitate is formed, $\overline{O}$ is present.</td>
</tr>
</table>

lates are absent; examine the solution in this case according to par. 193.

192. When the solution is attended with effervescence, add NH_4HO in excess to the solution, warm, and filter; the filtrate will contain the base or bases originally existing as oxalates; examine for these bases in the way directed in the second group, par. 68; wash the precipitate very well, then dissolve it in as small a quantity of boiling dilute HCl as possible; examine the solution according to par. 193.

193. Add one of the fixed alkalies in excess in the *cold* to the HCl solution; if FERRIC PHOSPHATE or OXIDE, or any of the PHOSPHATES OF THE ALKALINE EARTHS are present, they will be *precipitated,* whilst ALUMINIC and CHROMIC OXIDES and their PHOSPHATES will be retained in *solution;* examine the precipitate according to par. 195, and the solution according to par. 194.

194. *Boil* the fixed alkaline solution for some time; if a precipitate is produced, it is due to the presence of CHROMIC PHOSPHATE or OXIDE, or both; filter when a precipitate is produced, add to the filtrate, or to the solution, without filtering, when no precipitate has been produced,* acetic acid in excess; ALUMINIC PHOSPHATE, if present, will be precipitated; add to the filtrate NH_4HO in excess, when Al_2O_3, if present, will be precipitated. Dissolve the chromic precipitate in as small a quantity of boiling dilute HCl as possible, add an *alkaline acetate* in excess; CHROMIC PHOSPHATE, if present, will be precipitated; to the filtrate add NH_4HO in excess; if CHROMIC OXIDE be present, it will be precipitated.

195. After the precipitate produced by the fixed alkali has been well washed, it must be dissolved in as small a quantity of boiling dilute HCl as possible, then add one of the *alkaline acetates* in excess, and *boil* for some minutes; the FERRIC PHOSPHATE and OXIDE (the latter as basic acetate), will be *precipitated,* if present, whilst the PHOSPHATES OF THE ALKALINE EARTHS will

---

* If no precipitate is produced on boiling the fixed alkaline solution, a portion of the precipitate produced by the group reagent ought to be examined for chromium, in the way directed at par. 157.

remain in *solution;* examine the solution according to par. 196, and examine the precipitate for PO_4 in the following way:—Digest the precipitate in $(NH_4)_2S$ for a few minutes, then filter and examine the filtrate for PO_4, according to par. 424. To ascertain whether there was any Fe uncombined with PO_4, add to the original solution an *alkaline acetate;* filter, and to the filtrate add *potassic ferrocyanide.* If a blue precipitate is formed, it proves that all the Fe *did not* exist as phosphate.

196. To the solution add Fe_2Cl_6, drop by drop; if no precipitate is produced on the addition of the first two drops, the PHOSPHATES OF THE ALKALINE EARTHS *are absent;* if a precipitate is produced, continue the addition of the Fe_2Cl_6 until the solution is of a slightly reddish colour, then boil until the excess of Fe is removed from the solution by boiling, then filter, and examine the filtrate for Ba, Sr, Ca, Mg, in the usual way.

197. When substances are examined, the nature of which is a sufficient proof that the chromic oxide and phosphate, and the baric and strontic phosphates, and the baric, strontic and calcic oxalates must be absent, as in the case of soils, natural and artificial manures, &c.,* the last method may be much simplified;—the precipitate produced by the group reagent need not be ignited, the free alkali need not be added in the cold, and after its addition the mixture may be boiled, in order to hasten the filtration; and lastly, Ca and Mg have only to be sought for.

198. When substances are examined, the nature of which is a sufficient proof that calcic oxalate is the only oxalate, and that calcic and magnesic phosphates are the only phosphates of the alkaline earths which can be present, as in the case of *guano, urine, urinary deposits,* &c.,† a simpler method may be employed for detecting and separating these salts than the one given in Table V: after having separated them from all the

---

* Guano generally contains oxalate of lime; examine the ammonia precipitate of this manure according to par. 198.

† Of course in such substances as guano, urine, and urinary deposits, chromic oxide and its phosphate cannot be present.

other substances in the way directed in Table V, dissolve the precipitate produced by NH_4HO in the $H_2\bar{T}$ solution in a small quantity of HCl and to the solution add acetate of soda in excess. $Ca\bar{O}$, if present, will be precipitated, whilst the calcic and magnesic phosphates will remain in solution. Filter, and to the filtrate add $H_2\bar{O}$, which will precipitate the Ca existing originally as PHOSPHATE in the state of OXALATE. MAGNESIC PHOSPHATE will be precipitated from this filtrate on the addition of NH_4HO in excess.

199. The BORATES and FLUORIDES of BARYTA, STRONTIA, and LIME are also precipitated by NH_4HO; but they are not completely precipitated by NH_4HO in the presence of NH_4Cl: therefore, a portion at least of the bases of these salts will be found as a member of the second group, and the acids in these salts will be discovered in the ordinary examination of the acids, for these reasons we have not included these salts in the group; but it is necessary for the student to know that, when present in considerable quantities, they are in part precipitated by NH_4HO, as otherwise their precipitation along with the members of the 4th group might occasion him much perplexity.

Answers to the following exercises must be written out:—

EXERCISES.

87. What change does calcic oxalate undergo on being heated?

88. How would you examine a substance for baric and calcic phosphate?

89. If there were present in an acid solution $Ca\bar{O}$, $BaHPO_4$, $Fe'''PO_4$, and $Al'''PO_4$, and NH_4HO, and $(NH_4)_2S$ were added to it, which of the substances would be precipitated, and in what state would they be precipitated?

90. If there were present in an HCl solution $Ca\bar{O}$, $Fe'''PO_4$, $Al'''PO_4$, $CaHPO_4$, and sodic acetate in excess were added, which of the substances would be precipitated, and in what state would they be precipitated?

91. If you had a solution which could only contain calcic

oxalate, calcic phosphate and magnesic phosphate, devise a speedy method for the examination of these substances.

200. URANIC OXIDE (U_2O_3) *Solution of uranic nitrate in water may be employed for the reactions.* This oxide is of a brick-red colour, its hydrate is yellow; by ignition it loses part of its oxygen, being converted into U_3O_4, the colour of which is a very dark green, approaching black. U_2O_3 dissolves in acids, forming salts, the solutions of which have a fine yellow colour, and redden blue litmus paper. H_2S converts U_2O_3 into UO, which attracts O from the air, becoming converted into U_2O_3 again: oxidizing agents have the same effect.

201. $(NH_4)_2S$ *precipitates*, from alkaline solution of this oxide a brownish-coloured precipitate, which subsides slowly, and is readily soluble in acids, even in $\overline{HA}$; NH_4Cl promotes the formation of the precipitate.

202. The *volatile* and *fixed alkalies* precipitate this oxide from its solutions completely, in the form of a yellow precipitate, which is insoluble in an excess of the reagent.

203. $(NH_4)_2CO_3$ produces a yellow precipitate, which is soluble in an excess of the reagent, but is deposited again from this solution on boiling. In its behaviour with this reagent, U_2O_3 differs from Fe_2O_3, which it so closely resembles in its other reactions. $KHCO_3$ or $NaHCO_3$ produces a yellow precipitate which dissolves readily in an excess of the reagent.

204. K_4FeCy_6 produces in solution of this oxide a fine brown-red precipitate; this is a very delicate test for uranium.

205. " Uranium compounds give a yellow bead in the oxidizing flame, which becomes green in the reducing flame, especially on addition of $SnCl_2$. These colours closely resemble those of the iron compounds, but may easily be distinguished, at least if no other colouring metallic oxide is present, by the fact that the uranium bead, when incandescent, emits a bluish-green light, analogous to that which the uranium compounds exhibit when fluorescing. Beads of lead-oxide, stannic acid, and a few other substances, exhibit a similar phenomenon when incandescent, but they do not yield, like uranium compounds, a coloured bead on cooling.

206. " Heated gently on the platinum spiral with $KHSO_4$ the insoluble uranium compounds can be decomposed. The melted mass is powdered with a few particles of crystallized sodic carbonate, and the moistened mass is absorbed by filtering paper. A brown spot is formed by the addition of a drop of K_4FeCy_6 to the moistened paper."—*Bunsen.*

Characteristic.—The reactions with the caustic and carbonated alkalies and with K_4FeCy_6.

207. TITANIC OXIDE OR ANHYDRIDE (TiO_2).—This compound, although

comparatively a rare substance, occurs in some iron ores, and as it is considered by some to improve the quality of the iron, we have given, on this account, a short description of its properties, and the mode of detecting it.

208. It varies in colour according to the mode of preparation; it sometimes appears as a white powder, which, when heated, acquires during the time it is heated, a yellow tint, and sometimes it appears in the form of small lumps of a reddish-brown colour. The acid H_2TiO_3 is white. The anhydride is insoluble in water and acids, with the exception of concentrated H_2SO_4, which dissolves it with the aid of heat; when fused with $NaHSO_4$, the fused mass dissolves completely in a large quantity of cold water; when fused with Na_2CO_3, Na_2TiO_3 is formed, which is decomposed by H_2O into an acid salt, insoluble in H_2O but soluble in HCl and NaHO.

209. The acid in the moist state, and also when dried at a temperature not exceeding 100° C., is soluble in dilute acids, especially HCl and H_2SO_4. When the acid solutions of it are greatly diluted with water, and boiled for a long time, it, H_2TiO_3, is completely precipitated as a white powder, insoluble in dilute acids; this precipitate possesses the marked property of passing through the filter when washed, unless an acid or NH_4Cl is added along with it. It is precipitated from its acid solutions* in the form of a milky-white precipitate by the volatile and fixed alkalies and their carbonates, by $BaCO_3$, and by $(NH_4)_2S$; the precipitate is insoluble in an excess of the precipitant; but if it has been precipitated by any of these reagents in the cold, and washed with cold water, it is soluble in dilute HCl or H_2SO_4.

210. When the solution of titanic acid in HCl does not contain too much free HCl—when, for example, it has been prepared in such a way that part of the titanate treated by the HCl has remained undissolved, and has been filtered from the solution diluted with water—the solution of the acid behaves with the reagents named in *a*, *b*, and *c*, in the way described in these paragraphs.

(*a*) *Infusion of galls* produces in the solution a reddish orange-yellow precipitate of TANNATE OF TITANIC OXIDE.

(*b*) K_4FeCy_6 gives a dense orange-brown precipitate; the precipitate is soluble in an excess of the precipitant.

(*c*) White precipitates are produced by adding to the solution *dilute sulphuric, arsenic, phosphoric,* or *tartaric acid,* but more especially *oxalic acid;* these precipitates are completely redissolved in an excess of the precipitating acid, and likewise by HCl; the precipitate produced by H_2O is the most insoluble.

---

* Not in the presence of tartaric acid, or other non-volatile organic matter.

211. If a strip of ZINC, IRON, or TIN be introduced into a solution of titanic acid in HCl, the solution will become blue; and from this a reddish or violet precipitate will separate, which gradually oxidizes into the white oxide.

212. "Titanic compounds give a colourless bead with microcosmic salt in the oxidizing flame, which turns of a pale amethystine colour in the reducing flame. On addition of $FeSO_4$ the bead assumes in the reducing flame the peculiar red colour of venous blood, whilst in the oxidizing flame the light brown colour of Fe_2O_3 can be obtained at pleasure. The titanic compounds form with soda a bead, which at first effervesces, and when hot is colourless and transparent, but on cooling becomes opaque. If to the hot bead $SnCl_2$ be added, and if it then be heated in the lower reducing flame, a grey mass is formed, which dissolves on heating in HCl, yielding a pale amethystine-coloured solution."—*Bunsen.*

FIFTH GROUP.

STANNOUS OXIDE (SnO), STANNIC OXIDE (SnO_2), ANTIMONIOUS OXIDE (Sb_2O_3), ARSENIOUS ANHYDRIDE (As_2O_3), ARSENIC ANHYDRIDE (As_2O_5), AURIC OXIDE (Au_2O_3), PLATINIC OXIDE (PtO_2).

Solutions for the reactions.—$SnCl_2$, $SnCl_4$, As_2O_5, $PtCl_4$, $AuCl_3$, *in water;* $SbCl_3$, As_2O_3 *in dilute* HCl.*

213. *Examination for the members of the group.*—Auric and platinic compounds produce reactions so decisive—the former with the tin chlorides (284), and the latter with NH_4Cl (287)—that they may invariably be detected in the presence of all the other metals; they may, therefore, in all cases be sought for in the original solution. The examination of the precipitate produced by the *group reagent,* which must be added as directed at 357, is, therefore, confined to the other members of

---

* As no table is given with this group the student ought to perform the experiments given under the individual members before attempting the analysis of the group.

the group. Six different methods for the analysis of the group precipitate are given.

214. *First method.*—The group precipitate must be well washed, and then treated with a dilute solution of NH_4HCO_3.* As_2S_3 is soluble, and Sb_2S_3, SnS, SnS_2 are insoluble in NH_4HCO_3; filter if necessary, and add to the filtrate HCl in excess. If a *yellow* precipitate, or a slight yellow colour, is produced, As_2S_3 is present; the original solution must be examined to ascertain which of the two oxides of As is, or whether both are, present. The substance insoluble in NH_4HCO_3, after having been dried, must be mixed with three parts of fused NH_4NO_3, † and the mixture projected in small portions at a time into a porcelain crucible, containing two parts of NH_4NO_3 in a state of liquefaction. The ignition should be continued for a short time after all fuming has ceased, and the residue, when cold, must be treated with a *saturated* solution of $H_2\overline{T}$; if complete solution takes place, Sb_2O_3 only can be present; but if a portion remains undissolved, one or both of the *tin* oxides are probably present. Filter the $H_2\overline{T}$ solution when necessary, and add to the filtrate HCl and H_2S in excess; if an *orange-red* precipitate is formed, Sb_2O_3 is present. The substance insoluble in $H_2\overline{T}$ must be examined for Sn by fusing it with Na_2CO_3 and KCy, as directed at par. 236.

215. *Second method.*—Dry the precipitate, then treat it with boiling concentrated HCl; Sb_2S_3, SnS, and SnS_2 will dissolve with decomposition, whilst As_2S_3 will remain undissolved. Add a little water to the HCl solution, and pour it into a platinum crucible or lid, and introduce into it a piece of *pure* zinc, the Sn and Sb are reduced to the metallic state, and

---

* The solution is prepared by dissolving one ounce of NH_4HCO_3 in twelve ounces by measure of water; the precipitate must be agitated for a few seconds only with the solution, and then quickly filtered.

† When the amount of precipitate is so small that little or nothing can be detached from the filter, the precipitate as well as the filter, after having been cut into small pieces, must be mixed up with the ammonic nitrate, and subsequently projected into the crucible.

the latter blackens the platinum; when H ceases to be evolved remove the zinc, washing into the crucible or lid any reduced metal adhering to it, then free the reduced metal from the $ZnCl_2$ by washing, boil it in strong HCl, Sn will dissolve, whilst Sb will remain undissolved. Dilute the HCl solution a little, and then test it for Sn by adding to it $HgCl_2$ (235), or a mixture of Fe_2Cl_6 and $K_6Fe_2Cy_{12}$ (234); dissolve the portion of the metal insoluble in HCl in aqua regia, and test it for Sb by passing H_2S through the solution. Dissolve the portion of the sulphide insoluble in HCl in boiling HNO_3, evaporate nearly to dryness, add cold water, and test for H_3AsO_4 by adding NH_4Cl, NH_4HO, and $MgSO_4$ (277), or by adding $AgNO_3$ (275).

216. *Third method.*—Mix the dried *sulphides* with an equal quantity of Na_2CO_3 and a like quantity of $NaNO_3$; transfer the mixture gradually into a porcelain crucible containing twice the quantity of $NaNO_3$ *in a state of fusion*; when the deflagration is over* allow the crucible to cool; treat the fused mass with *cold* water and filter; wash the insoluble portion with equal parts of alcohol and water; filter the washings and mix them with the filtrate; add HNO_3 to the solution until it is distinctly acid; heat to expel CO_2 and N_2O_3 and test for H_3AsO_4 as directed in the second method; heat the insoluble residue with HCl; transfer to a platinum vessel, and test for Sn and Sb as directed in preceding par.

217. *Fourth method.*—Dissolve the sulphides in K_2S; add a concentrated solution of SO_2 in large excess, and digest the mixture in the water-bath for some time, then boil until all SO_2 is expelled, and afterwards filter; the filtrate will contain the As_2O_3, if present; test for it by passing H_2S into the solution; dissolve the insoluble portion in HCl and test it for Sb and Sn as in the second method.

218. *Fifth method.*—Dissolve the precipitated sulphides in as small a quantity of hot aqua regia as possible; introduce the

---

* The heat must not be too high nor continued too long, otherwise the $NaNO_2$ will be decomposed and caustic soda formed; and this latter will form with SnO_2 sodic stannate which will dissolve in the water.

solution into a hydrogen apparatus, along with some Zn and diluted H_2SO_4. The gas bottle must be connected with a second one containing a dilute solution of $Pb2\bar{A}$,* through which the gas in passing is freed from any HCl and H_2S. The exit tube from the wash bottle dips into a precipitating glass or test tube containing a solution of $AgNO_3$. If a precipitate is produced continue the transmission through the solution as long as it continues to be produced; then filter, carefully neutralize the HNO_3 in the filtrate with NH_4HO; the characteristic yellow Ag_3AsO_3 is precipitated. If the gas has passed through the solution for a long time the solution may contain no Ag. If, therefore, after neutralizing it no yellow precipitate is formed, add a drop or two of $AgNO_3$ to it. Wash the silver precipitate thoroughly with boiling water, and then boil it with a solution of $H_2\bar{T}$. Filter and acidify the filtrate with HCl, and pass H_2S through it; if Sb be present *orange-coloured* Sb_2S_3 will be produced. In order to detect Sn the metallic precipitate is washed off the Zn in the gas bottle and boiled in HCl; then diluted with a little H_2O, and tested for Sn by adding a solution of $HgCl_2$ (235).

219. *Sixth method.*—"If in a mixture of these three sulphides, containing only traces of Sb and Sn, they are separated according to the ordinary rules of qualitative analysis by dissolving in alkaline sulphides and reprecipitation with acids, the detection of these two metals by the regular tests is extremely uncertain and troublesome. According to the following method the detection of these metals is rendered easy and certain when the proportion of Sn is only a few thousandths, and that of the Sb only a few hundredths, of the total weight of the mixture.

220. "Three decigrammes of the sulphides are roasted on a curved piece of glass small enough to be altogether surrounded by the flame, and the residue, weighing only a few milligrammes, is scraped together with the knife. The moistened mass is then collected on the end of a thread of asbestos and

---

* A tube containing glass-splinters, moistened with a solution of $Pb(\bar{A})_2$, may be employed in place of the wash-bottle.

a strong metallic film obtained on the test tube. In order to prevent the deposition of any carbon with the metals, which would act injuriously in the subsequent operations, the upper reducing flame is made so small that the luminous point is only just visible. The film is next dissolved in a drop or two of HNO_3 in the curved rim (fig. 3) of the *Plate*, and the solution evaporated below its boiling-point by gently warming and blowing, so as to obtain the solid residue in as small a space as possible. A drop of neutral silver solution is now brought on to the residue at the moment when it becomes solid; and on blowing with ammoniacal air a characteristic black stain is formed, whilst the reaction of As is also generally noticed.

221. "In order to detect Sn, a few scarcely visible particles of the roasted sulphides are fused on to a borax bead which has been very slightly tinted with cupric oxide. If the bead is now brought into the lower reducing flame, it becomes a ruby-red colour from reduced cuprous oxide. If the oxide be present in too large a quantity, the bead can be obtained transparent by the process described under the reactions of the copper compounds. This reaction can only be obtained in the lower reducing flame of the non-luminous gas-lamp, as in the ordinary blowpipe flame, the cupric oxide is reduced to cuprous oxide without the presence of tin-salt."—*Bunsen*.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, AND THE HYDRIDES OF As AND Sb.

222. *The metals.*—As volatilizes at a dull red heat without previous fusion, its vapour is colourless and has a garlic odour. Sb melts at 432° C., and at a bright red heat volatilizes slowly, which is facilitated by transmitting a current of H over it. Sn melts at 228° C., and boils at a white heat; Au melts at above 1040° C.; Au and Sn are but slightly volatile in the heat of a furnace. Pt does not melt in the strongest forge fire, but it is fused and volatilized by the voltaic current, and in the oxyhydrogen blowpipe flame. Au and Pt suffer no change by exposure to air and moisture at any temperature. The other three metals undergo no change at ordinary temperatures in

dry air, neither in moist air does Sb suffer any change, but Sn tarnishes, and As slowly oxidizes; they all three unite with O if heated in the air, and at high temperatures burn with a brilliant light, As_2O_3, Sb_2O_3, and SnO_2 being formed. Sb and Sn decompose steam at a red heat. As decomposes it only slightly. Pt is not acted upon by any single acid, and selenic acid is the only one that acts on Au. HCl does not attack Sb, and has little action on As, but if heated it dissolves Sn, $SnCl_2$ being formed and H evolved. Dilute H_2SO_4 is without action on them, but boiling concentrated H_2SO_4 acts on them, SO_2 being evolved and As_2O_3, $Sb_2(SO_4)_3$, $Sn(SO_4)_2$ being formed; in the last case there is also a separation of S. Dilute HNO_3 converts As and Sb with the aid of heat into As_2O_3, and Sb_2O_3. The concentrated and boiling acid converts them into As_2O_5 and Sb_2O_5. HNO_3, if its sp. gr. is 1·5, does not act on Sn, but if it be diluted to 1·3 it acts violently upon it, converting it into metastannic acid ($H_2Sn_5O_{11}$, $4H_2O$), nitrous fumes are evolved, ammonia is also formed owing to the decomposition of H_2O. Aqua regia attacks all the five metals, converting them into $PtCl_4$, $AuCl_3$, $SnCl_4$, $SbCl_5$, and As_2O_5. Sb, As, and Sn combine readily with Cl, Br, I, P, and S; with some at ordinary, with others of them at higher, temperatures. Au combines directly with Cl, Br, and F, without the aid of heat, and with P when heated; dry Cl is without action on Pt; P and As combine with it when heated, forming phosphides and arsenides, which are very fusible; S also combines with spongy Pt, with the aid of heat. Chlorine water acts slowly upon Pt, and it converts Au into $AuCl_3$. The caustic alkalies do not affect Au, but the hydrates of the alkalies and alkaline earths, especially LiHO and BaH_2O_2, act on Pt if heated to redness with it in the air. It is even attacked at high temperatures by $KHSO_4$. As and Sn are also attacked by these hydrates at high temperatures;* in the case of Sn a metastannate is formed and H evolved; and in the case of As an arsenite and an arsenide are formed and H evolved. As and Sb, if in the form of an alloy, may be completely separated by heating the compound to low redness in a stream of CO_2, the As volatilizes whilst the Sb remains. Sb is the only metal which can be separated completely from As in this way, with all other metals a part of the As always remains combined. In their chemical relations these metals exhibit rather a chlorous than a basylous character, so that their oxides tend to unite with bases rather than with acids.

---

* When As is boiled in a strong solution of KHO, arsenite of potash is formed and H evolved.

223. *The oxides.*—SnO, SnO_2, PtO_2, As_2O_5 may be obtained by igniting with care their hydrates; As_2O_3 may be obtained by burning As in air or O, or by roasting arsenical ores; Sb_2O_3 by burning Sb in air; Au_2O_3 by adding to a solution of $AuCl_3$ MgO, and then dissolving out the MgO with HNO_3.[*] Au_2O_3 and PtO_2 are completely decomposed below a red heat, and As_2O_5 is resolved somewhat above its melting point into As_2O_3 and O. On being heated in air, SnO and Sb_2O_3 are converted into SnO_2 and Sb_2O_4; PtO_2 and Au_2O_3 are decomposed; As_2O_5 is converted into As_2O_3; SnO_2 and As_2O_3 are unchanged. As_2O_3, As_2O_5, SnO, SnO_2, and Sb_2O_3 are reduced to the metallic state on being heated in a current of H or CO, or if mixed with C or KCy; in the latter case potassic cyanate is formed. SnO, SnO_2, and Sb_2O_3, on being heated with S, are converted into the corresponding sulphides, SO_2 being evolved; As_2S_3 is formed on heating As_2O_3 with S, but a varying amount of As_2O_3 always escapes unconverted. If the oxides of Sn, Sb, and As are heated with NH_4Cl, chlorides of the metals are formed which volatilize; they are likewise converted into chlorides when heated in an atmosphere of Cl. PtO_2 and Au_2O_3 are reduced to the metallic state on being heated in an atmosphere of Cl. If As and Sb, or their sulphides, are diffused through a solution of KHO, and Cl conducted into the fluid, they are converted into arsenic and antimonic acids, which combine with some of the potash; SnO is converted into

---

[*] Magnesic aurate is precipitated, and on the addition of HNO_3 to the precipitate the MgO is dissolved, and the auric oxide is left in the anhydrous state if strong acid be employed, but in the hydrous state if the acid employed be weak.

SnO_2 by adding to its solution Cl. SnO, on being boiled in a small quantity of solution of KHO, is decomposed into Sn and SnO_2. The hydrates of these oxides may be obtained as follows:—$Sb_2O_3H_2O$ and 2SnO, H_2O by adding solutions of their chlorides to a solution of Na_2CO_3; H_2SnO_3 by adding to a solution of $SnCl_4$ an insoluble carbonate, as $CaCO_3$, in quantity insufficient for the entire decomposition of the chloride; PtO_2, $2H_2O$ by adding to a solution of platinic nitrate a solution of Na_2CO_3 in quantity insufficient for its complete decomposition; H_3AsO_4 by evaporating the arsenic solution obtained by oxidizing As_2O_3 with HNO_3; H_3AsO_3 is supposed to exist in solution, but it has never yet been isolated. Auric hydrate is obtained as directed in the note, page 90. As_2O_3, As_2O_5, and H_3AsO_4 are white; they are soluble in H_2O. SnO is black, $2SnO,H_2O$ is white; they are insoluble in H_2O. The hydrate is dissolved readily by acids, the anhydride is more slowly acted upon by them, the hydrate is soluble in the fixed alkalies, but if boiled with them is decomposed, SnO_2 remaining in solution, and Sn separating. SnO_2 is of a light straw colour, the hydrate is white; they are insoluble in H_2O; the anhydride is insoluble in acids, but forms soluble compounds with the alkalies; the hydrate is soluble in acids and the fixed alkalies. Sb_2O_3 and its hydrate are white; they are insoluble in H_2O, but soluble in HCl and $H_2\bar{T}$; their solution in this latter acid distinguishes them from the other anhydrous and hydrous oxides of the group; they are also readily soluble in solution of the fixed alkalies. HNO_3, or fusion with nitrates, converts Sb_2O_3 into a higher oxide. Au_2O_3 is of a deep brown colour; its hydrate is somewhat lighter in colour. PtO_2 and its hydrate are reddish brown. The auric and platinic oxides and their hydrates are readily soluble in HCl, but dissolve with difficulty in the oxygen acids.

224. *The sulphides* are formed, and in the amorphous state, on passing H_2S into a solution of their salts containing some free mineral acid,* with the exception of As_2S_5, as As_2S_3, with separation of sulphur, and not As_2S_5, is formed on passing

---

* Au_2S_3 is precipitated by H_2S from cold solutions of $AuCl_3$, but if the solution of $AuCl_3$ is boiling Au_2S is precipitated.

H_2S into acid solutions of As_2O_5. The amorphous Sb_2S_3, SnS, and SnS_2, obtained in this manner, are hydrated. As_2S_5 may be formed by adding HCl or other acid to a dilute aqueous solution of Na_3AsS_4, or any soluble sulph-arsenic salt. The following is the reaction:—

$$2Na_3AsS_4 + 6HCl = \underbrace{As_2S_5}_{\text{precipitated}} + 6NaCl + 3H_2S$$

Sb_2S_3 may be obtained in crystals by melting together at a red heat a mixture of S and Sb_2O_3. SnS may be obtained crystalline by heating Sn, in a finely-divided state, with S. SnS_2 may be obtained crystalline by heating a mixture of tin-filings, S, and NH_4Cl, or Hg, slowly to redness in a glass retort or loosely-covered flask. SnS_2 cannot be obtained by simply heating Sn and S, because the union is attended with such a development of heat that SnS_2 is resolved into SnS and S. A volatile substance, as NH_4Cl or Hg, is added to lower the temperature by rendering *latent* some of the heat evolved. The sulphides of this group are insoluble in H_2O, but soluble in the alkalies and alkaline sulphides. These sulphides possess acid characters; they, therefore, combine with the alkaline sulphides, which are basic, and form sulphur salts. When dissolved in the alkalies an oxygen, as well as a sulphur salt, is formed thus:

$$As_2S_3 + 6KHO = K_3AsS_3 + K_3AsO_3 + 3H_2O.$$

The solutions of these sulphides in the alkalies and alkaline sulphides are decomposed by the stronger acids, the sulphides reprecipitating, an alkaline salt of the acid added being formed, and when alkaline sulphides are employed H_2S being evolved. The members of this group are not precipitated by H_2S from alkaline solutions. Heated out of contact of the air, Au_2S_3 is decomposed into its elements, PtS_2 and SnS_2 are converted into the protosulphides, S being given off, Sb_2S_3, As_2S_5, and As_2S_3, melt below a red heat, and volatilize unchanged at a higher temperature. Heated in air,—Au_2S_3, and PtS_2, yield Au, Pt, and SO_2, SnS and SnS_2 yield SnO_2 and SO_2, As_2S_5 and As_2S_3 yield As_2O_3, and SO_2, Sb_2S_3, is converted into a fusible mixture of Sb_2O_3 and Sb_2S_3, which is of a red colour, and constitutes the commercial glass of antimony. Heated in a current of Cl, PtS_2 and Au_2S_3 are decomposed, Pt and Au remaining, As_2S_3, Sb_2S_3, SnS, and SnS_2, are converted into $AsCl_3$, $SbCl_3$, and $SnCl_4$, chloride of sulphur being also formed. Au_2S_3, PtS_2, Sb_2S_3, and SnS, are reduced, the latter only slowly, when heated in a current of H; As_2S_3 is only partly reduced by H. The sulphides of As, Sn, and Sb, are converted into their highest oxides on being fused with $NaNO_3$ and Na_2CO_3; the fused mass contains, if all these sulphides were present, SnO_2, sodic arseniate and antimoniate, with sodic sulphate, carbonate, nitrate and nitrite. Sb_2S_3 and As_2S_3, when heated in a current of steam, are partially oxidized, a sublimate composed of the oxide and sulphide in each case being formed, and H_2S evolved; if recently precipitated Sb_2S_3 and As_2S_3 are boiled in H_2O for some time, a small portion becomes decomposed, Sb_2O_3 and As_2O_3 being formed, and dissolved in the water, whilst H_2S is evolved. Dry HCl gas decomposes Sb_2S_3, but not As_2S_3; the $SbCl_3$ which is formed is very volatile in a current of the HCl gas. Recently precipitated As_2S_3 dissolves in $KHSO_3$ (the sulphides of Sn and Sb do not); if the solution is heated, SO_2 and S are set free, and there remain in solution $K_2S_2O_3$ and KH_2AsO_3; the following is the reaction:

$$2As_2S_3 + 16KHSO_3 = 6K_2S_2O_3 + 4KH_2AsO_3 + 4H_2O + 7SO_2 + S_3$$

Sb_2S_3 is decomposed by C with heat, Sb and CS_2 being formed, but As_2S_3 is not. If vapour of As_2S_3 or As_2S_5 be passed over heated Fe or Ag, or other metals, they are decomposed, the S combines with the heated metal, and the As is set free, which also combines with the reducing metal if it be in excess. Sn, Fe, Cu, and other metals, decompose Sb_2S_3 at a red heat by combining with the S, the liberated Sb combines with the reducing metal if it be in excess. If the sulphides of As, Sn, and Sb, are fused with KCy, the metals are obtained, and potassic sulphocyanide is formed. The arsenic sulphides are soluble in NH_4HO and in solutions of NH_4HCO_3, whilst the antimony and tin sulphides are almost insoluble in these reagents. The *colour of the sulphides and their solubility in acids.*—Crystallized Sb_2S_3 is *bluish-black*, the hydrated amorphous Sb_2S_3 is *orange red*, whether in the crystallized or amorphous state it is insoluble in dilute acids, but concentrated HCl dissolves it, $SbCl_3$ and H_2S being formed; concentrated H_2SO_4 decomposes it, yielding SO_2, S and a sulphate of Sb_2O_3; concentrated HNO_3 also decomposes it. Crystallized and amorphous As_2S_3, also called orpiment,* is lemon-yellow, concentrated and boiling HCl decomposes it only* very slightly; HNO_3 decomposes it, H_3AsO_4 and H_2SO_4 being formed; it is also decomposed by aqua regia. SnS in the crystalline form is bluish-grey, the hydrated amorphous SnS is chocolate-brown; it is insoluble in dilute acids; it dissolves in boiling HCl; boiling HNO_3 converts it into insoluble hydrate of metastannic acid. SnS_2 obtained in the dry way is a beautiful flaky compound, which is known under the name of mosaic gold; hydrated amorphous SnS_2 is faintly yellow; aqua regia is the only acid which decomposes mosaic gold, but the hydrated sulphide is not only decomposed by that acid, but also by boiling HCl, and also by concentrated HNO_3, which converts it into insoluble hydrate of metastannic acid. PtS_2 is blackish-brown, and Au_2S_3 is black; they are not attacked by HNO_3 or by HCl, but they are dissolved by aqua regia.

225. *The chlorides.*—$AsCl_3$,† $SbCl_3$, $SnCl_2$, and $SnCl_4$ may be obtained in the *anhydrous state* by distilling a mixture of the metals and $HgCl_2$. The following are the reactions:

(1) $2As + 3HgCl_2 = 2AsCl_3 + 3Hg$.

The $AsCl_3$ passes over into the receiver as an oily colourless liquid.

(2) $2Sb + 2\,HgCl_2 = SbCl_3 + SbHg + HgCl$.

(3) $Sn + HgCl_2 = SnCl_2 + Hg$.

The $SnCl_2$ remains behind as a grey brilliant mass, with a vitreous fracture; at a dull red heat it may be distilled.

---

* Realgar is a sulphide of arsenic, its formula is As_2S_2.

† There is no other compound of As and Cl known.

(4) $Sn + 2HgCl_2 = SnCl_4 + Hg_2$.

On the application of heat, $SnCl_4$ distils over as colourless liquid. $AsCl_3$, $SbCl_3$,* and $SnCl_4$, may also be prepared by passing a current of Cl over the metals or the sulphides, or by heating stannic or antimonious sulphate with NaCl, and by heating As_2O_3 with HSO_4 and NaCl. As Cl_3 is a dense transparent, oily, and volatile liquid, which does not solidify at 18° C., and boils about 132° C. It evaporates in the air at ordinary temperatures. $SbCl_3$ is a colourless, fusible, volatile solid, which is crystallizable and deliquescent; from its ready fusibility it was formerly known under the name of *butter of antimony*. $SnCl_2$ is a white, frequently grey solid, fusible, and volatile at a high heat. $SnCl_4$ is a transparent, colourless fluid, which does not congeal at — 29° C., and boils at 121° C.; it emits dense white fumes when exposed to the air, it absorbs water rapidly from the air, forming a terhydrate $SnCl_4$, $3H_2O$. These four chlorides are decomposed by H_2O, $AsCl_3$, if much water is added, is decomposed into As_2O_3 and HCl, but if only a small quantity is added, into ($AsCl_3$, As_2O_3) and HCl; $SbCl_3$ is soluble in a small quantity of H_2O, but in a large quantity it is decomposed into ($SbCl_3$ Sb_2O_3†) and HCl; if tartaric is added to the solution this decomposition is prevented. If hot water be added to a hot solution of $SbCl_3$ in HCl, it is decomposed into ($2SbCl_3$, $5Sb_2O_3$†), formerly called *powder of algaroth*, and HCl. $SnCl_2$ is decomposed, if mixed with a large quantity of water, into ($SnCl_2$, SnO, $2H_2O$) and HCl. $SnCl_4$ is readily soluble in a small quantity of water, but it is decomposed if much water be added into H_2SnO_3 and HCl; the precipitate of the antimony, stannous and stannic compounds is prevented if HCl be added along with the water. In the hydrated state $SnCl_2$ is obtained by dissolving Sn in HCl, the solution is usually effected in copper vessels on the large scale, since the voltaic opposition of the two metals favours the solution of the Sn; it crystallizes on evaporating the liquid in prismatic needles, the formula being $SnCl_2$, $2H_2O$. A solution of $SnCl_4$ may be prepared by dissolving stannic hydrate in HCl, or by treating a solution of $SnCl_2$ with Cl or by mixing $SnCl_2$ with HCl and treating it with HNO_3; when its aqueous solution is mixed with one of the alkaline sulphates, hydrated stannic oxide is precipitated thus:

---

* If the Sb is kept in excess, $SbCl_3$ is formed; but if the Cl is in excess, $SbCl_5$ is produced.

† By continued washing with water the chloride in these two compounds becomes removed and Sb_2O_3 only remains.

$SnCl_4 + 4Na_2SO_4 + 4H_2O = SnO_2, 2H_2O + 4NaCl + 4NaHSO_4$. Hydrated $SbCl_3$ is obtained in solution by dissolving Sb_2O_3 or $SbCl_3$ in HCl, the addition of tartaric acid to the solution prevents its decomposition by water; by evaporating the solution of Sb in HCl anhydrous $SbCl_3$ is obtained. As_2O_3 dissolves copiously in HCl; and if As_2O_3 or one of its salts is distilled with HCl of at least 1·1 density, $AsCl_3$ passes over with the aqueous acid, As may by this means be separated from most other metals and from organic matter; and the reaction explains the presence of As in hydrochloric acid made with oil of vitriol containing As; dilute solutions of As_2O_3 in HCl may be evaporated below 100° C. without any $AsCl_3$ volatilizing; but if the mixture be distilled to dryness in a retort, the $AsCl_3$ passes over with the last portions of the acid liquid. $SbCl_3$ combines with HCl and other chlorides, especially the alkaline chlorides, the general formula for which is $(M'Cl)_3\ SbCl_3$. $SbCl_3$ is employed for bronzing gun-barrels to prevent them rusting, the iron decomposes $SbCl_3$, and there is formed on the iron a covering of Sb. $SnCl_2$, 2 HO in crystals or in solution absorbs oxygen on exposure to the air, and forms a mixture of $SnCl_4$ and an oxychloride;* $SnCl_2$ has a strong attraction for Cl and for O, and is therefore a powerful reducing agent; it reduces gold, silver, and mercury salts to the metallic state; it converts ferric and cupric salts into ferrous and cuprous ones; it reduces chromic, manganic, arsenic, antimonic acids, &c., and the higher oxides of Pb and Bi, &c., into lower oxides; it reduces nitric acid to nitric or nitrous oxide, hypochlorous acid to chlorine; it deprives sulphurous acid of its oxygen; it converts indigo-blue into indigo-white; it is extensively employed as a mordant by the dyer and calico-printer under the name of *salts of tin*, and they also employ it for deoxidizing indigo and ferric and manganic oxides. It forms double chlorides with many of the chlorides of the alkalies and alkaline earths. $SnCl_4$ forms double salts with the soluble chlorides; the double salt $2NH_4Cl,SnCl_4$ is the *pink salt* of the dyer; an impure $SnCl_4$ is used by dyers under the name *nitro-muriate of tin*, *composition*, *physic*, or *tin solution*, it is used for brightening and fixing red colours. $PtCl_4$ and $AuCl_3$ are obtained by dissolving the metals in aqua regia, and evaporating the solution to dryness, the former by steam heat, and the latter at a temperature not exceeding 250° C.; in each case a red deliquescent mass is obtained, which is soluble in water, in alcohol and ether; these chlorides combine with other chlorides, forming double salts; they combine with most of the chlorides of the organic bases, they are therefore employed to determine the combining number of organic alkalies. They both give off Cl when heated, but Pt retains Cl much more tenaciously than Au. SO_2 and alkaline sulphites reduce $PtCl_4$ to $PtCl_2$, but those reagents precipitate Au from $AuCl_3$; this latter chloride is easily reduced by many substances, for instance, by P, by most metals, by *ferrous salts*, by oxalates, by As_2O_3 and Sb_2O_3, by many vegetable and animal substances. When Sn is digested in a neutral solution of $AuCl_3$, or a mixture of $SnCl_2$, and $SnCl_4$ very much diluted is added by degrees to a neutral solution of $AuCl_3$, a flocculent purple deposit called *purple of Cassius* is obtained. "The nature of this compound has been the subject of much discussion; Berzelius considered that it consists of a hydrated double stannate of gold and tin ($Sn''Au_2Sn_2O_3$, $4H_2O$); it is decomposed by acids, Au being left; it is unaffected by light; it is insoluble in the fixed alkalies, but soluble in NH_4HO, forming a deep purple solution, from which it is deposited unchanged if the ammonia be expelled by heat or neutralized by an acid. The ammonic solution is bleached by the action of light and Au is deposited. Purple of Cassius, when mixed with a little borax or some fusible glass, and applied to the surface of china, imparts to it a beautiful rose or a rich purple colour. It is this compound which is added as the colouring material in the red glass of Bohemia."

---

* The decomposition may be prevented and the solution kept clear, by the addition of HCl, $H\overline{T}$, or NH_4Cl, with which $SnCl_2$ forms a double salt not decomposable by H_2O or by exposure to air.

226. *Hydrides of* As *and* Sb.—As and Sb form with H gaseous compounds, viz., arsenuretted hydrogen AsH_3, and antimonuretted hydrogen SbH_3; these compounds may be prepared—1. By acting upon metallic arsenides and antimonides with acids:*

(1) $As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4$.
(2) $Sb_2Zn_3 + 6HCl = 2SbH_3 + 3ZnCl_2$.

2. By the action of nascent hydrogen, evolved, for instance, from Zn and H_2SO_4, upon soluble arsenic and antimony compounds:

(1) $As_2O_3 + 6Zn + 6H_2SO_4 = 2AsH_3 + 6ZnSO_4 + 3H_2O$.
(2) $SbCl_3 + 3Zn + 3HCl = SbH_3 + 3ZnCl_2$.

Fe and Sn act much less efficiently than Zn in producing these compounds. The SbH_3 is always mixed with free H. The H evolved from the negative pole of a battery of several cells converts As_2O_3 into AsH_3, but a weak current produces only a deposit of As; electrolytic H converts a portion only of the Sb of soluble antimony compounds into SbH_3, the remainder of the Sb being deposited in the metallic state on the negative plate.

227. The nascent H evolved by the action of KHO on Zn or Al, combines with As in arsenites forming AsH_3, but it does not act upon antimony compounds and form SbH_3; hence Fleitmann generates hydrogen in this manner to distinguish between As and Sb (par. 229).

228. AsH_3 and SbH_3 are colourless gases, the former has a most unpleasant odour, the latter is odourless; if passed through a heated tube they are decomposed into their ele-

---

* *Water* decomposes the compounds of the alkaline metals with As and Sb, AsH_3 and SbH_3 being formed along with the hydrate of the alkali.

ments, as they decompose below a red heat. When burnt in the air they yield H_2O and As_2O_3, and Sb_2O_3, respectively. If the supply of air is limited by depressing the *flame* with a piece of porcelain for instance, the H only is oxidized, the metal being set free is deposited on the porcelain, if cold. They are decomposed by Cl and by SO_2, HNO_3, aqua regia, and by all oxygenated acids, including strong H_2SO_4; they are also decomposed by solutions of mercury, and most other heavy metallic salts. They are decomposed when passed through concentrated HNO_3, H_3AsO_3, and H_3AsO_4, and Sb_2O_5 being formed. When passed through a solution of $AgNO_3$ the following changes ensue:

(1) $AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 3Ag_2 + 6HNO_3$.

(2) $SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3$.

229. If a solution containing H_3AsO_3, or an arsenite, be mixed with a large excess of a concentrated solution of KHO, and boiled with fragments of granulated Zn, H_3As is evolved, and may be readily recognised by allowing it to pass on to a piece of filter-paper moistened with a solution of $AgNO_3$; the paper assumes a purplish-black colour, even when a small quantity of arsenic is present. This test serves to distinguish As from Sb (*Fleitmann*).

230. As forms one other compound with H; it is a brown powder, and is obtained by passing an electric current through water, the negative pole being formed of metallic arsenic. Its formula appears to be AsH_2.

GENERAL CHARACTERS OF THE SALTS OF THIS GROUP.

231. Stannous salts are either colourless or possess a yellowish tinge, they have a disagreeable metallic taste, and rapidly abstract oxygen from the air and from oxygen compounds, and become converted into stannic salts. When largely diluted with water their solutions become *milky;* on the addition of a small quantity of HCl they are again rendered clear. Stannic oxide forms two hydrates distinguished as stannic

(H_2SnO_3) and metastannic hydrates ($H_2Sn_5O_{11}, 4H_2O$), the H_2SnO_3 is obtained by adding NH_4HO to a solution of $SnCl_4$; it is an amorphous gummy substance, soluble in HCl, HNO_3, H_2SO_4, $H_2\overline{T}$, and in KHO and NaHO, but not in NH_4HO. $H_2Sn_5O_{11}, 4H_2O$ is obtained by heating Sn or SnO with HNO_3, it is insoluble in $H_2\overline{T}$, and in HNO_3; when heated with concentrated H_2SO_4, it readily dissolves, forming a compound soluble in water, but on boiling the solution the compound is decomposed, the two acids separating. It is also insoluble in HCl, but it forms with it a compound insoluble in acids, but soluble in water; it is readily soluble in solutions of the fixed alkalies and their carbonates, but it is not dissolved by NH_4HO unless recently precipitated from a cold solution of its salts by the addition of an acid. By a heat of 284° C. stannic is converted into a metastannic acid, and the latter is converted into the former by fusion with an excess of caustic alkali. Both these acids unite with bases and form salts; the metastannates can exist only in the hydrated state, and those of potash and soda are the only ones soluble in water; the soluble stannates have a strong alkaline reaction, and their solutions absorb CO_2 from the air. Stannic hydrate dissolves in the stronger acids, forming stannic salts; these salts can also be prepared by adding to solutions of stannous ones an excess of acid, and then adding Cl or a small quantity of HNO_3. The stannic salts of the oxygen acids are very unstable. The acid properties of stannic hydrate are more powerful than the basic ones. Na_2SO_4, NH_4NO_3, and most of the neutral salts of the alkalies, if added in excess, and the solution be not too acid, precipitate from both the stannates and metastannates their hydrates. Some of the antimonious salts are decomposed by ignition, the haloid salts volatilize readily and unaltered; the antimony salts are decomposed when treated with a large quantity of water into *soluble acid* and insoluble basic salts; the basic salts are distinguished from the basic bismuth salts formed under like circumstances by being dissolved by a solution of $H_2\overline{T}$, in which the latter are insoluble. The hydrate $HSbO_2$* possesses more of the characters of a base than of an acid, nevertheless it can combine with bases. Potassic antimonious tartrate (tartar emetic) $KSbC_4H_4O_7$ is employed in medicine; it is prepared by boiling three parts of Sb_2O_3 with four parts of $KHC_4H_4O_6$ for about half an hour, renewing the water as it evaporates and filtering whilst hot; it is viewed by many chemists as containing the monatomic radical antimonyl (SbO); its formula according to this view is $K(SbO)'C_4H_4O_6$, and it is named potassic antimonylic tartrate. Arsenious acid unites with bases in several proportions; the arsenites are not very stable; the alkaline are the only arsenites soluble in H_2O, their concentrated solutions are decomposed by the CO_2 in the air; the insoluble arsenites are dissolved with decomposition by HCl. The arsenites of the metals of the alkalies and alkaline earths are decomposed by heat into arseniates, As being given off; plumbic arsenite is not decomposed by heat; the other arsenites are decomposed by heat, As_2O_3 being given off, and the metal left as oxide unless it is reducible by heat. Potassic arsenite is used in medicine under the name of *Fowler's solution*, and $CuHAsO_3$, and the double salt of arsenite and acetate of copper ($3CuAs_2O_3$, $Cu2C_2H_3O_2$), are employed as pigments, the first under the name of *Scheele's green* and the latter under the name of Schweinfurt or emerald green. Arsenic acid is a powerful acid, it takes away the bases from volatile acids; its salts have the general formula M'_3AsO_4; one or two atoms of M' can be replaced by an equal number of atoms of H; the alkaline arseniates are soluble in water, but the other arseniates are insoluble; most of the arseniates can bear a strong red heat without suffering decomposition. The salts of gold and platinum are decomposed on ignition. KHO, NaHO, NH_4HO, and their carbonates, produce in solutions of stannous salts a precipitate of SnH_2O_2, and in solutions of stannic salts a precipitate of stannic or metastannic hydrate, according to the nature of the solution; these different precipitates are soluble in an excess of KHO or NaHO, but are insoluble in an excess of the other precipitants; these reagents precipitate also Sb_2O_3 from solutions of $SbCl_3$, and also from other salts of Sb_2O_3, but from solutions of tartar emetic less completely, and only after the lapse of some time; the precipitate redissolves pretty readily in KHO or NaHO, but requires the application of heat for its solution in K_2CO_3, and is altogether insoluble in NH_4HO. Zinc precipitates from stannous, stannic, and antimonious solutions in the presence of free HCl, the metal; if the reduction takes place in a platinum vessel the part of the platinum covered by the liquid is stained brown or black by Sb but not by Sn; HCl does not remove the stain, hot HNO_3 removes it immediately. The members of this group are distinguished from those of the other groups by the solubility of their sulphides in the alkalies and alkaline sulphides; unlike the members of the previous groups, but like those of the sixth, they are precipitated from their acid solutions by H_2S.

---

* The normal hydrate H_3SbO_3 is not known.

REMARKS ON THE INDIVIDUAL MEMBERS OF THIS GROUP, WITH ADDITIONAL SPECIAL TESTS.

232. Sn *and its compounds.*—Sn has very little tenacity; it can easily be obtained in crystals; it is expanded by combined hammering and heating into sheets or leaves called *tinfoil.* SnO_2 occurs native as *tinstone* or *cassiterite;* this is the only ore of tin that is worked. Tin is a constituent of several important alloys. Speculum metal for the mirrors of reflecting telescopes, bell metal, and gun metal, are alloys of Sn and Cu; and the bronze used for coin consists of 95 pts. Cu, 4 of Sn, and 1 of Zn; solder is an alloy of Sn and Pb, and the amalgam of Sn and Hg is employed for the silvering of mirrors.

233. $AuCl_3$ produces, in solutions of stannous salts containing a small quantity of free HNO_3, a precipitate (purple of Cassius).

234. If a solution of a stannous salt is added to a mixture of $K_6Fe_2Cy_{12}$ and Fe_2Cl_6 Prussian blue precipitates immediately. This delicate test for a stannous salt can only be conclusive in cases where there are no other reducing agents present.

235. Solution of $HgCl_2$ produces in solutions of stannous

salts a white precipitate of HgCl, owing to the tin salt withdrawing half the Cl from the $HgCl_2$. If sufficient quantity of the tin salt be present, it removes, after a time, all the Cl from the Hg; the colour of the precipitate then becomes grey. Since this reaction takes place even in highly dilute solutions, and in the presence of much free HCl, it is very valuable for the detection of stannous compounds.

236. If Na_2CO_3 be mixed with equal parts of KCy and stannous or stannic compounds, and the mixed mass be subjected, upon a charcoal support, to the inner blowpipe flame, *ductile metallic grains of* TIN will be obtained, unaccompanied by any incrustation upon the charcoal.*

237. *On the charcoal splinter* the Sn compounds are easily reduced to white, lustrous, ductile, metallic beads. The flattened particles, transferred to the curved glass, slowly dissolve in HCl; and the solution, when absorbed by paper, gives a red precipitate with selenious, and a black precipitate with tellurous acid dissolved in HCl. If to the solution a trace of bismuth-nitrate be added, an excess of soda gives a black precipitate of Bi_2O_3. The metal, acted on by HNO_3, yields a white powder of insoluble SnO_2.

238. *A borax bead*, containing enough CuO to render it faintly blue, serves as a delicate test to ascertain with certainty the presence of a trace of a Sn compound, as the bead, placed in the lower reducing flame, turns reddish brown, or forms a clear ruby-red glass.—*Bunsen.*

239. Whether the Sn exists as a stannous or a stannic compound may be ascertained by adding to one portion of the solution $HgCl_2$, $AuCl_3$, or a mixture of $K_6Fe_2Cy_{12}$ and Fe_2Cl_6, and by adding another portion to a hot concentrated solution

---

* Bloxam has pointed out that if the KCy contains any K_2SO_4, the whole of the Sn is not obtained in the metallic state; if the quantity of K_2SO_4 is small, a portion of the Sn is converted into SnS, which separates as a *black* powder on treating the fused mass with H_2O; if there be much K_2SO_4, a portion of the Sn is converted into SnS_2, which is found in the aqueous solution of the fused mass, and from which it may be precipitated by HCl.

of Na_2SO_4. These, along with the blowpipe tests, are characteristic of Sn.

240. Another oxide, Sn_2O_3, is known. It is obtained as a slimy grey hydrate by boiling $Fe_2H_6O_6$ in a solution of $SnCl_2$:

$$2SnCl_2 + Fe_2O_3 = Sn_2O_3 + 2FeCl_2.$$

It dissolves in NH_4HO, which distinguishes it from SnO; and it is distinguished from SnO_2 by forming with $AuCl_3$ a purple precipitate. It does not appear to form definite salts.

241. Sb *and its compounds.*—Sb is a brilliant bluish-white metal. It is hard, and so brittle that it can be easily reduced to powder. It is inferior to most of the metals as a conductor of heat and electricity. In the state of fine powder it is easily dissolved by digesting it in a solution of a potassic polysulphide. If one part of tartar emetic is dissolved in four parts of a solution of $SbCl_3$, and the solution is subjected to the action of two or three cells of Smee's battery, using a plate of Sb for the positive, and a copper wire for the negative electrode, a metallic deposit of Sb, having the colour and lustre of highly-polished steel, and a bright metallic amorphous fracture, is deposited, the deposit retains 5 or 6 per cent. of $SbCl_3$. This amorphous Sb, when heated or struck, undergoes a rapid and intense molecular change throughout its mass, attended with great evolution of heat, increasing, at the same time, in density; it retains its cohesion and metallic aspect, but becomes grey, and acquires a granular fracture, and an increased density. The change is attended with an abundant disengagement of fumes of $SbCl_3$ (*Gore*). Sb is a constituent of several important alloys. It confers on these compounds hardness and the property of expansion in the act of solidification. Ordinary type metal is composed of 3 or 4 parts of Pb and 1 of Sb; the best is composed of 2 parts of Pb, 1 of Sn, and 1 of Sb. The principal mineral of Sb is the sulphide Sb_2S_3.

242. Introduce an antimonial solution into the apparatus (fig. 2), and add some Zn and dilute H_2SO_4, the presence of Sb in the evolved gas may be recognised by the following reactions:

1st. The gas will burn with a *bluish-green flame*, emitting white fumes of *teroxide of antimony*, which may be condensed in a cold beaker, dissolved in *hydrochloric acid* and tested with *hydrosulphuric acid*.

2nd. If the inner surface of a porcelain capsule be depressed upon the flame, a *black spot* of metallic antimony will be deposited upon it, which is lustrous, only when in thin layers. This deposit is distinguished from the similar arsenical stain by its solubility in solution of chloride of soda ($NaClO$), and by its ready solubility in $(NH_4)_2S$. Another method of testing the deposit is to moisten it with HNO_3 of Sp. gr. 1·42, then heat the vessel over a lamp, and blow over the surface to cause the acid to evaporate; the white deposit which remains will turn deep black with ammonio-nitrate of silver.

3rd. The glass tube from which the gas issues should be heated with a spirit lamp, in the centre; a *lustrous mirror of antimony* will be deposited on the inside of the tube, immediately around the flame of the lamp, whilst the bluish-green tint of the hydrogen flame in great measure disappears. The means for distinguishing this mirror from the arsenical one are given at pars. 262—2nd, and 263.

243. These reactions should be compared with those of terhydride of arsenic under similar circumstances.

244. If a solution of Sb_2O_3 in one of the fixed alkalies is mixed with a solution of $AgNO_3$, a deep-black precipitate of Ag_4O forms with the greyish-brown precipitate of Ag_2O. Upon now adding NH_4HO in excess, the Ag_2O is redissolved, whilst the Ag_4O is not (*H. Rose*). This very delicate test enables one to detect readily the presence of Sb_2O_3 in the presence of Sb_2O_5.

245. *Detection of* Sb *in organic mixtures.*—If it be in the solid state it should be cut up into small pieces; if it is a liquid, and in large quantity, it should by evaporation be reduced to a convenient bulk. It is then mixed with HCl and $KClO_3$, as directed at par. 733; from the filtered liquid the Sb may be precipitated by H_2S, or it may be introduced into the apparatus (fig. 2) and the gas tested for Sb, as directed in par. 242—1st, 2nd, and 3rd.

246. If compounds of Sb, mixed with Na_2CO_3 and KCy, be exposed, upon a charcoal support, to the reducing flame of the blowpipe, brittle grains of Sb will be formed, accompanied with a *white* incrustation on the charcoal.

247. *Flame coloration*, by treatment in the upper reducing flame, pale green, unaccompanied by any smell.

248. *Reduction film* black, sometimes dead, sometimes bright.

249. *Oxide film*, white; moistened with a perfectly neutral solution of $AgNO_3$, and then blown on by ammoniacal air, it gives a black spot which does not disappear in NH_4HO. If the film be first placed over bromine vapour the reaction cannot be obtained, owing to the oxidation of Sb_2O_3 into Sb_2O_5. It is unaltered by $SnCl_2$, either with or without NaHO.

250. *Iodide film* orange red, disappearing by breathing, and reappearing by blowing or warming; blown on with ammoniacal air it disappears, but does not return. Generally it gives the same reactions as the oxide.

251. *Sulphide film* orange red. The film is difficult to blow away with NH_4S_2; returns on blowing with air; insoluble in water.

252. *With soda on charcoal splinter* gives no black stain on silver, but yields a white brittle metallic bead.

Characteristic reactions.—The orange-coloured precipitate with H_2S, the *flame reactions*, and the decomposition of the neutral salts by water, and the solubility of the precipitate in $H_2\bar{T}$.

253. Two other oxides of Sb are known, viz. Sb_2O_4, which is generally regarded as composed of equal equivalents of Sb_2O_3 and Sb_2O_5, and is therefore named antimoniate of antimony. This oxide is obtained by heating strongly Sb_2O_5, which loses by the ignition one fifth of its O and becomes converted into Sb_2O_4, or it may be obtained by roasting Sb_2O_3 in the air. It is white, infusible, and unalterable by heat; slightly soluble in H_2O, more soluble in HCl; it is resolved into Sb_2O_3 and Sb_2O_5 on boiling it in a solution of $KH\bar{T}$. The other oxide is Sb_2O_5, it is called antimonic oxide, or anhydride, and is obtained by heating below redness one of its hydrates. It is

a yellowish powder insoluble in water and acids, but soluble in a solution of KHO; and when fused with K_2CO_3 the CO_2 is expelled, and potassic antimoniate is left. It appears to form three hydrates, forming three distinct acids thus: H_3SbO_4, the normal hydrate; $HSbO_3$, antimonic acid; $H_4Sb_2O_7$, metantimonic acid.

254. As *and its compounds.*—As has a brilliant dark steel-grey lustre. It is very brittle, and is easily reduced to powder. As_2O_3 is the arsenic, or *white arsenic*, of the shops. There are two varieties of this oxide, one, from its appearance is termed the vitreous, and the other the milky variety; when heated, they volatilize in white inodorous fumes. Both kinds are more easily soluble in hot than in cold water. As_2O_3 is exceedingly poisonous; and being altogether inodorous, almost destitute of taste, and readily obtainable, is frequently employed as a poison. The best antidote is the moist and well-washed ferric hydrate. *Arsenic anhydride* (As_2O_5) is a white solid; it has no action on litmus paper; is nearly insoluble in H_2O and in NH_4HO; it fuses at a low red heat without undergoing decomposition, but at a higher temperature it is resolved into O and As_2O_3, which volatilizes. *Arsenic acid* (H_3AsO_4) is readily soluble in water, and it may be obtained in large transparent crystals by exposing a concentrated solution to a very low temperature. Its aqueous solution dissolves Zn and Fe with evolution of H; but if H_2SO_4, or HCl, is present it is reduced and converted into H_3As. SO_2 passed through a solution of it reduces it to As_2O_3, H_2SO_4 being formed. The greater part of As_2O_3 of commerce is prepared from mispickel (FeAsS), an arsenical sulphide of iron furnished abundantly by the Silesian mines; and from the arsenides of Ni and Co, which yield As_2O_3, as a secondary product in the ordinary process of working these ores. In the manufacture of shot a small quantity of As is added to the Pb to facilitate its assuming the globular form.

BEHAVIOUR OF As_2O_3 AND THE ARSENITES WITH REAGENTS.

255. $AgNO_3$ produces in neutral solutions of the arsenites a yellow precipitate of Ag_2HAsO_3, soluble in HNO_3 and NH_4HO; $AgNO_3$, therefore, produces no precipitate, or only a slight turbidity in solutions of As_2O_3, but on neutralizing the acid with NH_4HO the precipitate appears. Ammonio-nitrate of silver is, therefore, a more appropriate reagent than $AgNO_3$ if the acid be free.

256. $CuSO_4$ produces in neutral solutions of the arsenites a yellowish-green precipitate of $CuHAsO_3$ soluble in NH_4HO, and in acids; $CuSO_4$ produces, therefore, no precipitate in solutions of As_2O_3, but on neutralizing the acid with NH_4HO the precipitate appears; ammonio-sulphate of copper is, therefore, a more suitable reagent than $CuSO_4$ in testing an acid solution.

257. If to a solution of As_2O_3, or an arsenite, solution of KHO be added in excess, and a few drops only of a *dilute* solution of $CuSO_4$, and the liquid subsequently boiled, a red precipitate of Cu_2O will fall down, whilst the solution will contain POTASSIC ARSENIATE. This test is particularly applicable in distinguishing As_2O_3 from As_2O_5. It cannot be employed with safety as a direct means for detecting As_2O_3, as many organic substances possess the property of reducing CuO to the state of Cu_2O.

258. "If to As_2O_3, no matter whether in the solid form or in solution, some $HC_2H_3O_2$ is added, and then KHO in slight excess, the mixture evaporated to dryness, and the residue heated to redness in a small tube—or if a trace of As_2O_3 is introduced into a narrow test-tube, and there covered with a somewhat larger quantity of $NaC_2H_3O_2$, and heat applied—part of the As_2O_3 is reduced, but there forms at the same time ALKARSIN (oxide of cacodyl) $2(As(CH_3)_2)O$, which makes its presence immediately known by its equally characteristic and formidable odour, which somewhat resembles that of sharp onions. This changes speedily to the not less characteristic

odour of chloride of cacodyl ($As(CH_3)_2Cl$), if the ignited contents of the tube are heated with a few drops of $SnCl_2$.—*Bunsen.*

259. If arsenites, or As_2O_3, or As_2S_3, are fused together with a mixture of equal parts of dry Na_2CO_3 and KCy, the whole of the As, and also the base, if an easily reducible one, is reduced to the metallic state, the O converts part of the KCy into KCyO. In the reduction of As_2S_3, KCyS is formed. The operation is conducted as follows:—Introduce the perfectly dry arsenic compound into the bulb of a small bulb-tube, and cover it with six times the quantity of a perfectly dry mixture of Na_2CO_3 and KCy. The whole quantity must not more than half fill the bulb, otherwise the fusing KCy is likely to ascend into the tube. Apply the heat of a lamp to the bulb, and continue this for a while, as the As frequently requires some time for its complete sublimation. The metallic mirror is deposited on the cold part of the tube of exceeding purity; and is obtained from all arsenites whose bases remain either altogether untouched, or are reduced to arsenides which lose their As partly or totally upon the application of heat. By this method minute quantities of As can be detected, and it is especially adapted for obtaining As from As_2S_3. The delicacy is increased by heating the mixture in a stream of dry CO_2, as described in the next par.

260. The apparatus (fig. 1) consists of a flask A capable of holding about eight or twelve fluid ounces; it is fitted with a funnel-tube, and a bent tube which dips into a smaller flask, B. In A CO_2 is slowly generated from pretty large fragments of marble (no powder) and dilute HCl; it is conveyed into B, which is partly filled with concentrated H_2SO_4, in order to dry the gas. The exit-tube from B is bent at right angles, and connected, by means of a cork, with the reduction-tube; this latter tube is made out of a piece of hard glass tube (combustion-tube) somewhat more than three eighths of an inch in diameter, and drawn out at one extremity to a long point; the length of the body of the tube should be about four inches, that of the point at least two and a half inches.

261. A mixture of 3 parts of anhydrous Na_2CO_3 and 1 part of KCy is dried in the water bath; about 12 parts of this dried mixture is mixed with 1 part of As_2S_3, or the arsenite, which has been also dried in the water-bath; the mixture, before it has time to get damp, is put upon a narrow slip of card-paper bent into the shape of a gutter; it is then introduced into the tube, and the latter is turned half round upon its axis; the mixture falls upon the glass, and the gutter is withdrawn. The mixture should be in the middle of the tube, and it ought not to occupy more than an inch. The reduction-tube must now be fixed, by means of the cork, to the exit-tube of B, and a moderate stream of CO_2 ought to be evolved, by pouring some HCl into A, by means of the funnel-tube. Heat the reduction-tube, in its whole length, very gently with a lamp, until the mixture is perfectly dry; when all the water is expelled, moderate the gas stream so that only one bubble shall pass through the H_2SO_4 in B in a second; the gas stream may be moderated by pouring water into A. When the gas stream is moderated, apply the flame of a lamp to the shoulder of the tube; and when this part of the tube is red hot, apply the flame of a second lamp, commencing at the end of the reduction-tube nearest B, and heating along up to the mixture; continue to apply the flame at the part where the mixture is, until all the As is expelled. The far greater portion of the volatilized As recondenses in the narrow part of the tube, whilst an extremely

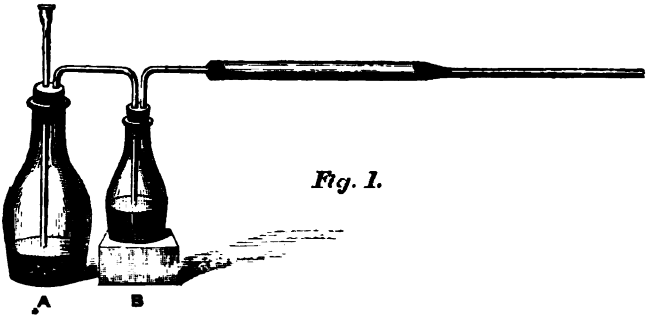


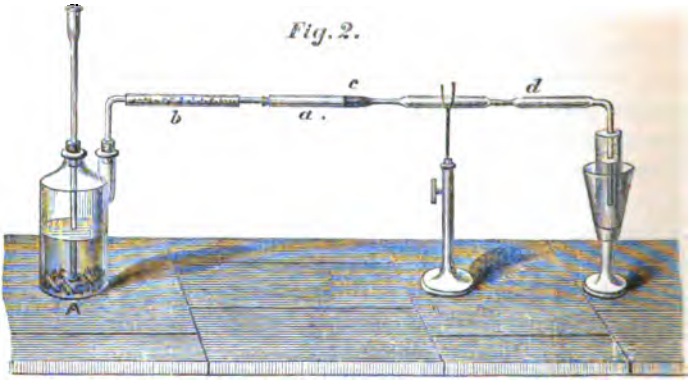
Fig. 1.

minute portion only escapes through the fine point, imparting to the surrounding air the peculiar odour of garlic. Advance the flame of the second lamp slowly and gradually up to the first, by which means the whole of the As which may have condensed in the wide part of the tube is driven into the narrow part. When this end has been attained, close the fine point of the tube by fusion, and apply heat, proceeding from the closed point towards the part where the greater part of it is condensed, by which means the extent of the mirror is narrowed, whilst its beauty and lustre are correspondingly increased. In this manner, perfectly distinct mirrors of As may be produced from as little as the one-hundredth part of a grain of As_2S_3. No mirrors are obtained by this process from Sb_2S_3, nor from any other compound of Sb.

262. *Marsh's test for Arsenic.*—The apparatus (fig. 2) is a convenient one, as the AsH_3 can be both tested by reagents, decomposed in the tube by heating the tube, and the AsH_3 may also be burnt as it escapes from the opening of the tube, and the As deposited in the tube and the As_2O_3 produced by burning the gas can each be tested. A is a flask for the acid, the Zn, and the solution to be tested. It is provided with a funnel-tube for conveying the liquids. b is a tube filled with fragments of fused calcic chloride for drying the gas. c.d. is a tube of hard-glass (free from lead) about one quarter of an inch in diameter, and having, as shown in the figure, two or three capillary contractions, and bent at a right angle, so that it may form a jet, or that it may dip into a solution of $AgNO_3$.

The first thing to be ascertained is whether the Zn and dilute H_2SO_4 to be employed are free from As; for this purpose they must first be introduced into A, *without* the solution to be tested, and after the evolution of the H has continued long enough to expel all the air, the tube is to be heated at *a* for about five or ten minutes, and the escaping gas conducted into a solution of $AgNO_3$. If no deposit is produced in the tube or a precipitate in the Ag solution, the Zn and H_2SO_4 are free from As, and the solution to be examined for As may be introduced into A,* and the evolved gas then examined in the following manner:

Fig. 2.



1st. Hold a piece of filter-paper, moistened with a solution of $AgNO_3$, over the open end of c.d.; if H_3As is present the paper will assume a *purplish-black colour.* Inflame the gas, if H_3As is present it will burn with a *livid blue flame,* producing a white smoke of As_2O_3; condense the As_2O_3 by holding a wide, cold, test-tube over the flame; dissolve the condensed matter in hot water, and test it for H_3AsO_3, especially with ammonio-nitrate of silver, and with H_2S, after acidifying with HCl.

2nd. Heat the tube at *a* by means of a lamp, As will be deposited a little beyond the flame as a steel-grey ring; after a sufficient deposit has been obtained at that point, remove the lamp to the next division and obtain a second deposit; if necessary, a third may be obtained in the third division. Let the escaping gas during the heating of the tube pass into a solution of $AgNO_3$; when the operation is over the portions of the reduction-tube containing the deposits may be cut off with a file and the deposits examined. The As deposit is soluble in a solution of chloride of soda (NaClO, and it is perceptibly dissolved if a drop of $(HN_4)_2S$ be added to it. If the crust be dissolved in concentrated HNO_3, and evaporated just to dryness upon a sand-bath, a little water added, and afterwards ammonio-nitrate of silver, a ***brick-red precipitate*** of Ag_3AsO_4 will be obtained; an antimony spot, when treated in this way, generally gives a slight dirty white precipitate with the Ag solution. The $AgNO_3$ solution, through which the gas has been passed, ought to be examined for As as in the fifth method (par. 218).

---

* If there is much frothing when organic matter is present, a little alcohol must be added to prevent it.

263. Another method for distinguishing which of the two metals, As or Sb, has produced the mirror, and also for distinguishing and detecting the two metals when they occur together, is the following:—Having obtained the mirror in the tube c.d. in the manner already described (par. 262—2nd), a feeble stream of dry H_2S must be transmitted through the tube, the metallic mirrors being gently heated from their outward to their inward border. If only As be present, the yellow sulphide As_2S_3 will be formed. If Sb only be present, the orange or black Sb_2S_3 will be produced; but if both metals be present, the two sulphides will be formed; and the As_2S_3, being the more volatile of the two, will be the further removed from the flame. A stream of dry HCl gas must be passed through the tube without the application of heat; by this means the Sb_2S_3 will be converted into volatile $SbCl_3$, which will entirely disappear, whilst the As_2S_3 will remain unaltered, and may be distinguished from any sulphur which may have separated, by dissolving readily in NH_4HO.

264. In employing Marsh's test for the detection of As it is necessary, as has already been stated, to have the solution free from Cl, HNO_3, $HClO_3$, SO_2, aqua regia, mercury salts, &c. SO_2 may be present if the organic matter has been carbonized by H_2SO_4, and the presence of SO_2 may give rise to the production of H_2S by the action of the nascent H upon it; H_2S may also be formed if the H_2SO_4 is not sufficiently diluted to prevent its acting too violently upon the Zn. H_2S must not be present, because it would form with the arsenic As_2S_3, which is not converted by the H into AsH_3. In conclusion, it may be remarked that the presence of organic matter sometimes

completely prevents the detection of minute quantities of As by Marsh's method.

265. If clean metallic copper is boiled in a solution containing As_2O_3, acidified with HCl, the copper becomes coated with a *steel grey film* of As; if the quantity of As_2O_3 is considerable, the reduced As will separate from the Cu, when the liquid is boiled for some time, in *large black scales*. As many other metallic oxides are reduced to their metallic state under the same circumstances, it is necessary to submit the crust to further examination. This test, which is called "Reinsch's test," is particularly useful for the detection of As in organic liquids or solids. "The suspected liquid is simply to be acidulated with about one sixth of its bulk of HCl, and boiled. The solid tissue must be cut up into very small pieces, and boiled for some time in a mixture of about one part of HCl with six of water, until the whole is disintegrated; then strained through muslin, or filtered through a previously wetted filtering paper.

266. "Into either of the above boiling liquids dip the end of a piece of clean polished copper wire; examine the wire from time to time, and as soon as its surface acquires a grey metallic discoloration remove it, and add in its stead fragments of fine copper gauze, continuing the supply as long as the last added piece assumes any definite alteration in colour.

267. "Remove the pieces of copper gauze, wash them in water, and dry them between folds of filtering paper; the deposit will not rub off unless the amount of As be very large. If the As exist in but very small quantity, the colour of the precipitated metal is bluish; otherwise, of a dark iron-grey tint. Holding the piece of gauze in the fingers, warm it over a flame, coil it up into a small compass, and introduce it into a reduction-tube: now apply heat cautiously; the As will volatilize, oxidize, and condense in the cold part, in the form of a white crystalline sublimate. Several pieces of coated gauze may be thus treated successively, until a sufficiently obvious sublimate of As_2O_3 is procured; by examination with a lens, or with the low power of a microscope, the crystals will be seen

to consist of highly iridescent octo- and tetra-hedra." File off the piece of tube containing the sublimate, boil it for a minute or two in a little water; test the water after the boiling for As_2O_3, one portion with HCl and H_2S, and another portion with ammonio-nitrate of silver.

268. As is not deposited on the Cu in the presence of oxidizing bodies, and the HCl in their presence dissolves the Cu. When present they must be got rid of by reduction or other means before introducing the copper foil or gauze. As a small quantity of Cu is always dissolved, the foil or gauze employed should be at least so far free from As that a solution of four or five grains of it should not yield a perceptible trace of it. The HCl to be employed should also be free from As; its purity may be conveniently ascertained by diluting it with three or four times its own volume of water and boiling in it, for some time, a piece of the copper foil to be employed; if pure, the Cu will not be stained. We may observe, in conclusion, that the arsenical film which peels off from the Cu is not pure As, but an arsenide of copper (Cu_5As_2). On heating the copper foil in the tube only a portion of the As, and relatively only a small portion, volatilizes, the rest of it remains behind united with the Cu.

269. *Detection of* As *in organic mixtures.*—Before examining for arsenic in articles of food and dead bodies it is necessary in the generality of cases to destroy the organic matter before attempting to search for the arsenic compound, as, from its consistence, &c., it impedes the application of the reagents or masks their reactions; the destruction involves the use of chemical reagents, which as far as possible ought to be avoided, on account of the difficulty of obtaining many of them perfectly free from arsenic; as by the *dialytic* method no chemical reagent of any kind is introduced into the organic mixture, it is desirable first to dialyse the suspected organic matter; for this purpose the solid portion is cut into small pieces, the mixed solid and liquid portion is then placed in the dialyser* to

---

* The dialyser ought to be about ten inches in diameter, and perfectly sound. See the Author's 'Second Step in Chemistry,' p. 681.

the depth of not more than half an inch, the dialyser is then floated in a basin containing a volume of water about four times greater than the organic fluid. After twenty-four hours about three fourths of the As_2O_3 (or other crystalloid poison) will be found in the water of the basin, which is generally colourless. To this liquid, after concentration on the water-bath, all the ordinary tests of arsenic may be applied.

270. *Destruction of the organic matter.*—Sulphuric acid, hydrochloric acid and potassic chlorate, chlorine, aqua regia, nitric acid and potassic nitrate, sulphuric acid and sodic chloride, have been respectively proposed and recommended by different chemists for the destruction of the organic matter in the examination for arsenic in medico-legal cases; we shall describe a few of these methods.

1st. The organic matter, after it has been minutely divided, is mixed with about a fifth of its weight of *pure* concentrated H_2SO_4, and heated for some time, continually stirring with a glass rod; the mass becomes brown and finally black, and white fumes of H_2SO_4 are evolved along with SO_2; the heat must be continued, but not so high as to volatilize any arsenic, until the residue is reduced to a *dry friable* carbonaceous mass; it is then pulverized, and afterwards treated with a small quantity of concentrated HNO_3 for oxidizing As_2S_3, which may have been contained in the suspected matter, or which may have been formed by the simultaneous reduction of H_2SO_4 and the As_2O_3 during the carbonization; the mixture is again evaporated to dryness to expel completely the HNO_3; it is then boiled in water and filtered, and the filtrate examined for arsenic by Marsh's test. The employment of H_2SO_4 was proposed by MM. Flandin and Danger. The process is open to some objections; some NaCl will always be present in the organic matter, and under certain conditions $AsCl_3$ will be formed by the reciprocal reaction of the H_2SO_4, the NaCl and the As_2O_3; the $AsCl_3$, if formed, will volatilize, and consequently escape detection;* it is also very difficult to obtain H_2SO_4 perfectly free from arsenic.

* To avoid this loss it has been proposed to conduct the operation in a

2nd. The employment of HCl and $KClO_3$ for the destruction of the organic matter possesses many advantages; it is certain, and in the examination other metallic poisons as well as arsenic can be sought for and detected, and it allows of a quantitative determination of the poison; the process is described in par. 733.

3rd. M. Schneider has proposed to separate the arsenic from the organic matter with which it is mixed by converting it into the volatile $AsCl_3$; for this purpose the organic mixture under examination is introduced into a retort (fig. 3) and a quantity of NaCl added, and then through the safety tube a little at a time some pure concentrated H_2SO_4; the mixture is then distilled, the receiver being kept cool; the three-bulb tube connected with it contains distilled water. It is necessary to keep the NaCl in the retort in excess, to prevent the formation of SO_2, when the liquid becomes concentrated in the retort. As $AsCl_3$ is decomposed by H_2O, it cannot be formed when there is much of that liquid present; if the organic mixture contains much water it ought, therefore, to be con-

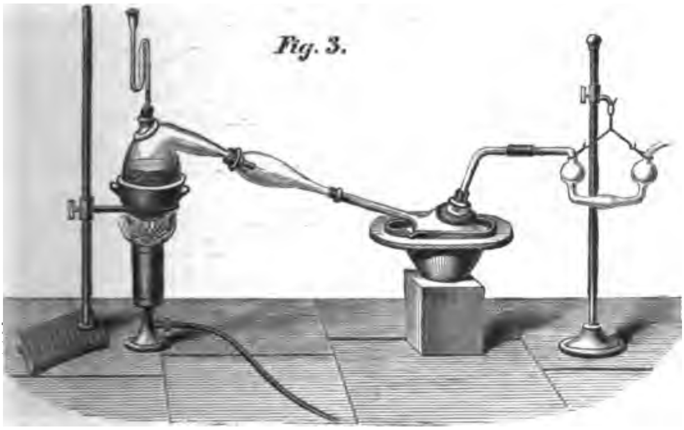


Fig. 3.

retort, and collect any matter that distils over in water, but this modification renders the method less simple and convenient.

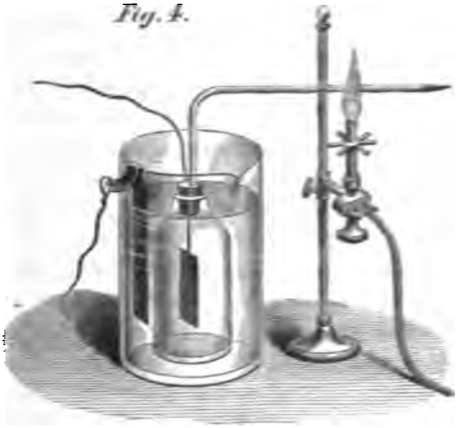
centrated by distilling it by the aid of the water-bath before adding the NaCl and H_2SO_4. The distillate is diluted with water and treated with H_2S, and the As_2S_3 is reduced by KCy (259), or it is converted into As_2O_5 by means of HNO_3; the excess of the latter being expelled, the As is detected by means of Marsh's method.

271. Bloxam has proposed to employ the electric current for the conversion of As into H_3As. This, the electrolytic method of eliminating arsenic, possesses certain advantages over that of Marsh:—1. It avoids the use of Zn, and thereby obviates a frequent source of error arising from the presence of As in that metal. 2. It introduces no substances into the liquid that can interfere with its subsequent examination for other metals. If any other metals are present it precipitates them on the surface of the negative plate. When the AsH_3 is obtained by means of Zn, Sb, if also present, is evolved together with the As, and the subsequent separation of these two metals is troublesome; but with the electrolytic method only a very small quantity of Sb is evolved as SbH_3, and even this quantity may be completely arrested by adding to the liquid a solution of H_2S. Both Sb and As are then converted into sulphides, but the As_2S_3 is converted by the electrolytic hydrogen as easily as As_2O_3 into AsH_3, whereas the Sb_2S_3 completely resists the action of it, and consequently remains in the liquid.

272. The apparatus consists of a two-ounce narrow-mouthed bottle, the bottom of which has been cut off and replaced by a piece of vegetable parchment, tightly stretched over it and secured by a ligature of thin platinum wire (a ligature of organic matter is quickly destroyed). The bottle is furnished with a cork, in which is fitted air-tight a quill tube bent at right angles; also a platinum wire, to which is attached a plate of the same metal, which forms the negative pole of the voltaic circuit; it is also convenient to have fitted in the cork, although it is not shown in fig. 4, a funnel tube for introducing the liquid to be tested. The bottle is placed within a glass of such a size as to leave a small interval between the

two, and this glass is allowed to stand in a vessel of cold water. About an ounce of dilute H_2SO_4 is introduced into the apparatus, so as to fill the bottle and the outer vessel to about

Fig. 4.



the same level, the positive plate being immersed in the acid in the outer vessel. The current of a voltaic battery (six Grove's cells of ordinary size) is then passed through the arrangement, and when the bottle has become filled with hydrogen the tube is heated to redness during fifteen minutes, to ascertain the purity of the H_2SO_4; the liquid to be tested is then introduced into the bottle by means of the funnel tube, or by a pipette, the cork being removed for an instant; a drachm of alcohol is also added to prevent frothing; the heating of the reduction tube is then continued for thirty minutes before the absence of arsenic is inferred.

273. The following method has been recommended by Bloxam for the detection of poisonous metals by electrolysis, viz.—The mixture, which may, of course, have been previously examined for organic poisons by the usual methods, is digested on a water-bath, with so much water, HCl and $KClO_3$, as may be required to disintegrate the solid organic portions, and to render the liquid capable of filtration; the filtrate is evaporated on the water-bath to a small bulk; it is then treated with an

excess of H_2S water, and introduced into the decomposing cell along with some alcohol, to prevent frothing; and the passage of the current is continued for about an hour. In the heated tube the As, if present, will be found, and on the negative plate and in the liquid the other poisonous metals will have to be sought for. 1st. As regards the tube, the As, if H_2S or SO_2 has been introduced into the decomposing cells, is deposited either in part or entirely as As_2S_3 in the tube a little beyond the heated portion; there is generally a deposit also of As, and if an excess of H_2S has been employed a deposit of S, which is nearer the orifice than the deposit of As_2S_3, and from which it may easily be distinguished by its much lighter colour, and by its insolubility in a warm solution of NH_4HCO_3, which readily dissolves As_2S_3. It is probable that the deposit of As_2S_3 is occasioned by the AsH_3 and H_2S reacting upon each other under the influence of heat. If H_2S is added, and no As is present, a thin white film of S will generally be deposited in the tube. 2nd. If no H_2S has been employed, the metals to be sought for on the negative plate are Sb, Hg, Cu, and Bi; the plate having been washed, is boiled in somewhat dilute yellow $(NH_4)_2S$ for a minute or two. This solution is then evaporated on a watch-glass placed in the water-bath, and the orange residue of Sb_2S_3 identified by the usual tests. The platinum plate having been again washed, is boiled in a few drops of concentrated HNO_3, to which a drop of dilute HCl should be added to dissolve the HgS. The acid solution is boiled down to a small bulk and mixed with an excess of NH_4HO, by which the presence of Cu will be rendered evident, and the Bi_2O_3 will be precipitated, together with a little $2NH_4Cl, PtCl_4$. To examine for Bi the precipitate is dissolved in HCl evaporated and largely diluted with H_2O. The filtered ammoniacal liquid, acidulated with HCl, and boiled with clean copper, will prove the presence or absence of Hg. If H_2S has been added, this plan will have to be modified, as the Sb_2S_3 and other sulphides which have been formed will be found suspended in the liquid of the decomposing cell, and not deposited in the metalline state on the negative plate.

274. *Flame reactions.*—1. *Flame-coloration* in upper reducing flame pale blue, giving the well-known arsenical smell.

2. *Reduction-film* black, dead or brilliant, thin film brown.

3. *Oxide-film* white; touched with a perfectly neutral solution of $AgNO_3$, and then blown with ammoniacal air, it gives a canary-yellow precipitate, soluble in NH_4HO. Together with this yellow precipitate, a brick-red one of silver-arseniate occurs when the film has previously been treated with bromine vapour. $SnCl_2$, with and without soda, produces no change.

4. *Iodide-film* is deep yellow, disappears on breathing, but returns on drying; disappears in ammoniacal air, and does not return; reappears unaltered after the action of HCl.

5. *Sulphide-film* lemon-yellow, disappears easily on blowing with $(NH_4)_2S$, and reappears on warming or blowing; insoluble in H_2O, and does not disappear by breathing.

6. *Reduction on charcoal splinter* yields no metallic bead.

BEHAVIOUR OF ARSENIC ACID AND THE ARSENIATES WITH REAGENTS.

275. $AgNO_3$ produces, in neutral solutions of the arseniates, a characteristic reddish-brown precipitate of Ag_3AsO_4, soluble in dilute HNO_3 and in NH_4HO; $AgNO_3$ produces, therefore, no precipitate, or only a slight turbidity in solutions of H_3AsO_4, but on neutralizing the acid with NH_4HO the precipitate appears; ammonio-nitrate of silver is, therefore, a more appropriate reagent than $AgNO_3$ if the acid be free.

276. $CuSO_4$ produces, in neutral solutions of the arseniates, a greenish-blue precipitate of $CuHAsO_4$.

277. $MgSO_4$, in the presence of NH_4Cl and of NH_4HO, produces, in solutions of the arseniates, a white precipitate of $MgNH_4AsO_4$, soluble in acids.

278. H_3AsO_4 produces, not only with magnesian salts, but also with ferric salts and with ammonic molybdate, precipitates similar in appearance and in constitution to those produced by these reagents with H_3PO_4, but it is distinguished from this

latter acid by the colour of its silver salts, and by its conversion into As_2S_3 on being treated with H_2S.

279. Nascent H, evolved by the action of Zn on dilute H_2SO_4 or HCl, converts H_3AsO_4, as it does As_2O_3, into H_3As, but the conversion is much slower, and in those reactions which depend upon the reduction to the metallic state H_3AsO_4 resembles As_2O_3.

280. Whether As exists as As_2O_3 or as H_3AsO_4 may be ascertained by testing a portion of the original solution with the copper test (257), and another portion of the original solution with the silver (275) or magnesian test (277).

281. Au *and its compounds.*—Au is the only metal of a yellow colour. It unites with nearly all the metals, but its most important alloys are those which it forms with Ag and Cu. The standard gold for coin in England contains 8·33 per cent. of Cu. In France and the United States it contains 10 per cent. of Cu. Jewellers frequently alloy their gold with Ag as well as Cu; the Ag gives it a lighter colour. The solder used for gold trinkets is composed of 5 parts of Au and 1 part of Cu, or of 4 parts of Au, 1 part of Cu, and 1 part of Ag. Gold is always found in the metallic state generally more or less alloyed with Ag.

282. Ferrous salts precipitate Au from its solutions as a *bluish-black* precipitate, which acquires a metallic lustre when rubbed.

283. A solution of $SnCl_2$ and some $SnCl_4$ produces, even in very dilute solutions of Au, a purple precipitate (purple of Cassius), the tint of which varies according to the quantity of Au present. The precipitate is insoluble in *dilute acids;* the Au solution should be first mixed with the $SnCl_4$, and the $SnCl_2$ then added drop by drop. When the quantity of Au is extremely minute, a *pink tinge* pervades the solution.

284. A very delicate method of applying this test is as follows:—Fe_2Cl_6 is added to $SnCl_2$ until a permanent yellow colour is produced; the solution is then considerably diluted; the Au solution, having likewise been much diluted, is poured into a beaker, which is placed on a sheet of white paper; a

glass rod is dipped into the Fe solution, and afterwards into the Au solution, when, if even a trace of Au be present, a *blue or purple streak* will be observed in the track of the glass rod. This test has the advantage of being applicable even in very acid solutions.

285. One other oxide of gold is known, viz. the aurous oxide, Au_2O. It is a green powder, and is obtained by decomposing $AuCl_3$ with a cold solution of KHO.

286. Pt *and its compounds*.—Pt in compact masses is white, but in a finely divided state, obtained by precipitation, it is as black as soot, and is termed *platinum black*. It is obtained as a grey, porous, slightly coherent mass, called spongy platinum, by igniting the double chloride of $2NH_4Cl, PtCl_4$. Pt possesses the valuable property of uniting when two masses of it are pressed or hammered together at a high temperature. This operation of uniting masses of metal into one is termed "welding." Wollaston, who first devised a process of working Pt, made use of this property. He purified the Pt from other metals by boiling it in HNO_3. He then dissolved it in aqua regia, and converted it into $2NH_4Cl,PtCl_4$. From this salt he obtained "spongy platinum." This was heated, compressed, and hammered until it became homogeneous and ductile, and had a sp. gr. of about 21·5. Deville and Debray have lately proposed a new plan. They dissolve out the Pt from its ore by liquid Pb, which does not dissolve the impurities. The Pb is subsequently separated from the Pt by cupellation, and the Pt is finally melted in a crucible of lime by means of the oxyhydrogen blowpipe. "The most important applications of Pt are confined to the laboratory of the manufacturing and experimental chemist; they depend upon its great infusibility and its power of resisting chemical reagents. Pt always occurs in the metallic state, usually in small flattened grains, in which it is mixed with palladium, rhodium, osmium, ruthenium, and iridium—metals which are rarely found except when associated with Pt."

287. KCl or NH_4Cl produces, in solutions of Pt, a yellow crystalline precipitate of $2KCl, PtCl_4$, or $2NH_4Cl, PtCl_4$. The

presence of HCl promotes the formation of this precipitate. Dilute solutions should be evaporated along with the KCl or NH_4Cl and the HCl on the water-bath to dryness, and the residue digested in weak spirits of wine until the excess of the alkaline chloride employed is dissolved.

288. Solutions of platinic salts produce, in solutions of $SnCl_2$, which contain much HCl, a dark *brownish-red colour;* in exceedingly dilute solutions the colour is *yellow*, and becomes darker on standing. This test is a very delicate one for Pt. The dark brown colour is owing to the reduction of the platinic to a platinous salt.

289. Platinum forms with oxygen another oxide, viz. platinous oxide (PtO).

290. Answers to the following exercises must be written out.

EXERCISES.

92. Give the results of the action of $Fe''SO_4$ and of $H_2\bar{O}$ on $AuCl_3$.

93. Give the theory of the method of Marsh for the detection of As.

94. How would you distinguish the product of the action of H_2O on $SbCl_3$ from the similar one produced on $BiCl_3$ by H_2O?

95. Describe by equations the reactions which take place when H_2S is passed into a solution of arsenious acid, through one of arsenic acid, and through one of tartar emetic.

96. Describe by equations the reactions which take place when a stannous salt is added to a mixture of $K_6Fe_2Cy_{12}$ and Fe_2Cl_6, and to a solution of $HgCl_2$.

97. For what purposes is Pt employed in the metallic state, and how is it obtained in mass?

98. Describe the method proposed by Schneider for separating As from organic matters.

99. For what purposes is Sb employed in the arts in the metallic state?

100. Describe by an equation the reaction which takes place when a mixture of As_2O_3, KHO, and acetic acid is

evaporated to dryness, and the residue heated, and what is the name of the arsenic compound which is produced.

101. Describe the dialytic method of separating crystalloid poisons from the contents of the stomach.

102. I have got some copper nickel, NiAs, containing some $CoAs_2$, and I wish to prepare some pure nickel: how shall I proceed?

103. Give an account of the method of employing electrolysis for the separation of As and Sb from liquids containing organic matter.

104. Give the composition of tartar emetic, a method for preparing it, its properties, and the action of chemical reagents upon it.

105. How would you convert arsenious acid into arsenic acid, and reconvert the latter acid into the former one; and how would you distinguish solutions of these acids from each other?

106. Describe the changes which take place when As_2S_3 is digested with H_2SO_3 and $KHSO_3$.

107. Describe by an equation the changes which take place when H_3As and H_3Sb are passed through a solution of $AgNO_3$.

108. What is the action of reagents upon argentic and cupric arsenite, and how would you detect the metals including As in these compounds?

109. Describe by an equation the changes which take place when a solution of an arsenious compound, KHO, and fragments of Zn are boiled together.

110. How do you account for the presence of As in HCl?

111. How are gun-barrels bronzed?

112. How would you detect and how remove the oxides of nitrogen and As_2O_3, so often present as impurities in sulphuric acid?

113. To what acid is the term aqua regia applied? and describe its chemical properties.

SIXTH GROUP.

ARGENTIC OXIDE (Ag_2O), MERCUROUS OXIDE (Hg_2O), MERCURIC OXIDE (HgO), BISMUTHOUS OXIDE (Bi_2O_3), PLUMBIC OXIDE (PbO), CUPRIC OXIDE (CuO), CADMIC OXIDE (CdO).

For the reactions.—$AgNO_3$, $HgNO_3$, $HgCl_2$, $Pb(NO_3)_2$, $CuSO_4$, $CdCl_2$ or $CdSO_4$—*dissolved in* H_2O; $BiCl_3$ *dissolved in dilute* HCl.

291. The insolubility of AgCl, HgCl, the slight solubility of $PbCl_2$, and the ready solubility of the other chlorides, enables one to divide this group into two sections.

First section.—The oxides which form with HCl insoluble chlorides are the members of this section. They are Ag_2O, Hg_2O, and PbO.

Second section.—The oxides which do not form with HCl insoluble chlorides are the members of this section. They are HgO, Bi_2O_3, CuO, CdO, and PbO, as the slight solubility of $PbCl_2$ in water renders it impossible to confine this member exclusively to the first section—a portion of the $PbCl_2$, varying according to the amount of liquid present, always remaining dissolved; the Pb it contains is precipitated along with the members of the second section on the addition of H_2S. If attention be paid to the following facts, they will frequently remove a source of much confusion:—1. If Pb has been discovered in the first section, a precipitate must always be obtained on passing H_2S through the filtrate, even if no other member of the group be present. 2. If only a small quantity of Pb be present, HCl may cause no precipitate, as a sufficient quantity of water may be present to dissolve the chloride formed. In this case all the Pb will be found in testing for the members of the second section.

292. *Examination for the members of the first section.*—When a solution is examined for the members of this group only, the general reagent for this section must be added, as

directed at par. 355; and when a precipitate is produced, it must be washed as there directed, and then examined according to the method described in next par.

293. Add *boiling water* to the precipitate; $PbCl_2$ will be dissolved, if present, which is ascertained by H_2SO_4 producing in the filtrate a precipitate of $PbSO_4$. If a residue remain after removing the $PbCl_2$ by adding successively to the mixed chlorides fresh quantities of boiling water, until the last washings give on the addition of H_2SO_4 no further precipitate, it proves that either AgCl or HgCl, or both, must be present. NH_4HO being added to the residue, dissolves the AgCl, whilst it converts HgCl into the *black* mercurous ammonic compound. To detect the AgCl in the ammonic solution, HNO_3 must be added in excess, which, by neutralizing the solvent, causes the AgCl, if present, to be re-precipitated.

294. *Examination for the members of the second section.*—When a solution is examined for the members of this group only, the general reagent must be added as directed at pars. 357 and 358, and when a precipitate is produced it must be washed until the last washings contain no trace of Cl;* it must then be examined according to the next par.

295. The washed precipitate must be boiled in *dilute* HNO_3. If it all dissolves, with the exception of a light yellow mass of sulphur, HgO is absent; but if, after boiling for some time, the undissolved mass presents a black appearance, it points out the probable presence of that member. Examine the black mass for HgO, as directed in par. 296. To the acid solution, after it has been filtered from the yellow or black mass, and subsequently evaporated nearly to dryness, so as to remove the greater part of the free acid, must be added a little water, and then a few drops of *dilute* H_2SO_4, which will precipitate the Pb as $PbSO_4$ after the lapse of a longer or shorter time; the solution must therefore be allowed to stand some

---

* The removal of the Cl is ascertained by the wash-water giving no precipitate on the addition of a few drops of a solution of $AgNO_3$; the wash-water to be tested must not be collected with the previous washings, but by itself, and in a *clean* test-tube.

TABLE VI.

BEHAVIOUR OF THE MEMBERS OF THE FIRST SECTION WITH THE SPECIAL REAGENTS.

(PbO.)	(Ag_2O.)	(Hg_2O.)
P 1. $PbCl_2$ is difficultly soluble in *cold water*; it is much more soluble in *boiling water*. It is precipitated by H_2SO_4 from its aqueous solutions as $PbSO_4$, which is insoluble.	Q 1. AgCl is insoluble in *water*.	R 1. HgCl is insoluble *in water*.
P 2. $PbCl_2$ is very slightly soluble in NH_4HO; the ammonic solution becomes turbid after a short time, from the separation of the lead as an insoluble oxychloride ($PbCl_2$, 3PbO, + H_2O), which is soluble in HNO_3; it is therefore easily distinguished from AgCl.	Q 2. AgCl is easily soluble in NH_4HO. On the addition of any acid in excess it is again precipitated from this solution.	R 2. HgCl does not dissolve in NH_4HO, but becomes altered in colour, the *white chloride* being converted into a *black compound*, di-mercurous ammonic chloride (Hg_2H_2NCl).

BEHAVIOUR OF THE MEMBERS OF THE SECOND SECTION WITH THE SPECIAL REAGENTS.

(HgO.)	(PbO.)	(Bi_2O_3.)	(CdO.)	(CuO.)
S 1. HgS is *black*; it is *insoluble* in boiling HNO_3, but is easily soluble in aqua regia.	T 1. PbS is *black*; it is *soluble* in boiling HNO_3.	U 1. Bi_2S_3 is *black*; it is *soluble* in boiling HNO_3.	V 1. CdS is *yellow*; it is *soluble* in boiling HNO_3.	W 1. CuS is *black*; it is *soluble* in boiling HNO_3.

S 2. $HgSO_4$ is decomposed, in the presence of much water, into an insoluble basic and a soluble acid salt.	T 2. H_2SO_4 precipitates, from solutions of lead, $PbSO_4$, which is *insoluble* in water and dilute acids, freely soluble in ammonic acetate and tartrate.	U 2. H_2SO_4 produces no precipitate in solutions of this oxide, $Bi_2(SO_4)_3$ being *soluble* in water.	V 2. H_2SO_4 produces no precipitate in solutions of this oxide, $CdSO_4$ being *soluble* in water.	W 2. H_2SO_4 produces no precipitate in solutions of this oxide, $CuSO_4$ being *soluble* in water.
S 3. NH_4HO* produces, in solutions of $HgCl_2$, a WHITE PRECIPITATE ($Hg_2H_4N_2Cl_2$), *insoluble* in an excess of the reagent.	T 3. NH_4HO throws down, from solutions of plumbic salts, white basic salts, which are insoluble in an excess of the reagent.	U 3. NH_4HO throws down, from solutions of Bi, the HYDRATE, *insoluble* in an excess of the reagent.	V 3. NH_4HO precipitates, from solutions of Cd, CdH_2O_2, *soluble* in an excess of the reagent.	W 3. NH_4HO produces, in solutions of this oxide, a GREENISH BLUE precipitate, which *dissolves* with a beautiful azure colour in an excess of the reagent.
S 4. $(NH_4)_2CO_3$† behaves in the same way, in solutions of Hg'', as NH_4HO.	T 4. $(NH_4)_2CO_3$ precipitates, from solutions of Pb, $PbCO_3$, *insoluble* in an excess of the reagent.	U 4. $(NH_4)_2CO_3$ throws down, from solutions of Bi, a WHITE BASIC CARBONATE, *insoluble* in an excess of the reagent.	V 4. $(NH_4)_2CO_3$ throws down, from solutions of Cd, $CdCO_3$, *insoluble* in an excess of the reagent.	W 4. $(NH_4)_2CO_3$ behaves in the same way in solutions of Cu as NH_4HO.

---

* The fixed alkalies precipitate all the members of this group from their solutions; the lead precipitate is difficultly soluble in an excess of the reagents; all the rest are insoluble. The precipitate produced by the fixed alkalies, in solutions of the Hg'', is the yellow oxide, unless ammonic salts are present; in that case the precipitate is the same as that produced by NH_4HO.

† The fixed alkaline carbonates precipitate all the members of this group from their solutions. If added to cupric solutions in the cold, they produce a basic carbonate; but if the solution is boiled, it is converted into CuO.

time before NH_4HO is added. NH_4HO being added in excess to the filtrate, throws down the Bi (confirm its presence according to par. 324). The filtrate from the ammonic precipitate, or the solution with which that reagent has failed to give a precipitate, is divided into two parts, which we shall call A and B.

A. The A portion is acidulated with acetic acid and tested for Cu, if the presence of that metal has not been already manifested by the blue colour of the ammonic solution, by adding to it K_4FeCy_6; if Cu *is present*, a brownish-red coloured precipitate will be produced; if Cu *is absent*, the colour of the solution will not be altered by the reagent (346).

B. The B portion, when Cu is absent, is examined for Cd in the following manner:—$(NH_4)_2S$ is added to the ammonic fluid, and if it produces a *yellow precipitate* Cd is present.

When Cu *is present*, the B portion is examined for Cd in the following manner:—Add a small quantity of dilute H_2SO_4 to the solution and evaporate it to dryness and ignite, continuing the ignition until the ammonic salt is expelled; then add a *concentrated* solution of NH_4HCO_3, and boil for a short time; *if no precipitate* is produced, Cd is absent. *If a precipitate is produced*, wash it with the NH_4HCO_3 solution until all the Cu is removed; then dissolve the residue in a little dilute HCl, and afterwards add NH_4HO in excess, and finally *one* drop of $(NH_4)_2S$; if a *yellowish precipitate*[*] is produced on the addition of the $(NH_4)_2S$, Cd is present.[†]

If Pb has not been discovered in either section, the black or light-coloured precipitate insoluble in HNO_3 ought to be digested in $NH_4\bar{A}$ and filtered, to the filtrate add $H\bar{A}$ in excess, and then a solution of K_2CrO_4; if Pb is present, a yellow precipitate, $PbCrO_4$, will be formed.

---

[*] The reason for recommending the addition of only one drop of $(NH_4)_2S$ is this—a small quantity of Cu frequently remains undissolved by the NH_4HCO_3; in such case, if only a drop of $(NH_4)_2S$ be added, the Cd, if present, will be first precipitated; whereas, if more $(NH_4)_2S$ were added, the Cu would also be precipitated, and consequently obscure the Cd. When the colour of the precipitate produced by $(NH_4)_2S$ is black or of a doubtful colour, it must, after being washed, be dissolved in HNO_3, the solution must be evaporated to dryness, and the residue treated as before with the concentrated solution of NH_4HCO_3, &c.

[†] For other methods for the separation of Cd and Cu see par. 352.

296. If a black residue remain after boiling the mixed sulphides in HNO_3, it must be collected upon a filter, to separate it from the other members, and specially examined for HgO by one of the two following methods:—1st. After having dried the black mass thoroughly in a water bath, mix it with dry Na_2CO_3, and proceed with the examination for Hg in the way described in par. 319. 2nd. Dissolve the black mass in as *small a quantity* of AQUA REGIA *as possible*, or dissolve it by heating it with HCl and a few crystals of $KClO_3$, then add NH_4HO in slight excess, and then a slight excess of HCl; examine the solution, thus prepared, for Hg by means of copper wire, in the way described at par. 314 or 315.

297. *The following precautions must be attended to in analysing this group*:—The means, both for separating and detecting the members of the first section, are so simple and positive, that no difficulty will be experienced by the student. It may, nevertheless, be as well to observe, that $PbCl_2$ ought to be completely removed before NH_4HO is added, for if it is not, a *white residue*, which is nothing more than $PbCl_2$, may remain after the addition of NH_4HO, when Hg is absent, which may perplex the student. And if the $PbCl_2$ be not completely removed before the addition of NH_4HO, the ammonic solution will appear turbid, owing to the separation of an insoluble basic salt of lead: this will not, however, interfere with the test for Ag, since it (the basic salt of lead) redissolves upon the addition of HNO_3. The difficulties which occur in examining the second section will be easily overcome by a little attention. Many erroneous conclusions will be formed if the simple yet necessary precaution of washing the H_2S precipitate be neglected, because a small quantity of the HCl employed to precipitate the first section, being left behind, will form with the HNO_3 aqua regia, which, by dissolving the HgS, may cause that member to be overlooked; and should the mercury thus pass into solution, a compound of that metal will

be precipitated on the addition of NH_4HO, which may be mistaken for Bi. The precipitate must, therefore, before it is treated with HNO_3, be washed with water until the wash-water, acidulated with HNO_3, gives no precipitate with $AgNO_3$. It is difficult to free the mass of sulphur, which separates on the addition of HNO_3, entirely from some of the undecomposed sulphides, which, by communicating to it a black appearance, might lead to the belief that HgO was present, even in the absence of that member. An experienced eye can generally distinguish between this mixture of undecomposed sulphide and sulphur, and HgS, the former being light and flocculent, whilst the latter is dense and heavy; but a safe and legitimate conclusion can only be arrived at by examining it specially for Hg. A varying amount of H_2SO_4 is always formed by dissolving the sulphides in HNO_3: a portion of the Pb will therefore be precipitated as sulphate, and remain behind mixed with the substance insoluble in HNO_3; it is necessary, on this account, to examine the insoluble mass for this member, if it should not be met with in its proper place. As $PbSO_4$ precipitates from dilute solutions, and especially from those which contain much free acid, only after the lapse of some considerable time, the solution ought, after the addition of H_2SO_4, to be allowed to stand for a considerable time (an hour) before adding the NH_4HO. A precipitate will be formed on the addition of NH_4HO to the solution in HNO_3, if either of these reagents contains a trace of Fe, but this precipitate cannot be mistaken for Bi if the confirmatory test be applied.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, THE SULPHATES OF THIS GROUP.

298. *The metals.*—None of the metals of this group, when perfectly pure, oxidize in *dry* air or oxygen at *ordinary* temperatures; in *moist* air or oxygen Pb, Bi, Cu, and Cd* undergo a

---

* Pb, Bi, and Cd oxidize if exposed to the combined action of air and water.

slight superficial oxidation; these four metals oxidize rapidly on exposure to air or oxygen at a *red heat*, PbO,* Bi_2O_3, CuO and CdO being formed. Ag does not oxidize in air or O at any temperature; Hg oxidizes at 371° C., HgO being formed; at 427° C. the oxide is decomposed into its elements. Ag, Hg, Pb do not decompose H_2O, even at a very elevated temperature; Bi and Cu decompose it slightly at elevated temperatures, and Cd decomposes it at a red heat. Cd is the only metal in this group which can displace the hydrogen in H_2SO_4; the action takes place even when the acid is dilute, $CdSO_4$ and H_2 being formed; the dilute acid, and even the undiluted acid in the cold, has no action on the other metals,† but if they are boiled in the undiluted acid they become oxidized, sulphates of the metals, H_2O and SO_2, being formed.‡ HCl *in solution* has no action on Hg, and it only acts on Ag, Pb, Bi, and Cu when they are boiled in it, and even then very slowly §; it acts readily on Cd, $CdCl_2$ and H_2 being formed. HCl in the gaseous state acts on Ag and Cu, when they are heated to redness in it, a chloride of the metal and H_2 being formed. HNO_3 oxidizes and dissolves all the metals of this group, a nitrate of the metal being formed, and generally NO (nitric oxide) is the other nitrogen compound produced; but the degree of reducing action which these and other metals exercise on HNO_3 varies with the *strength* of the acid and the *temperature;* for example, when Ag is acted upon by dilute HNO_3 in excess at ordinary temperatures, $AgNO_3$ and HNO_2 (nitrous acid) and the anhydride are formed, but at higher temperatures the oxide of nitrogen formed is NO. When Cu and Hg are acted upon by HNO_3 of moderate concentration,

---

[*] At a low red heat red lead (2PbO, PbO_2) is formed.

[†] If copper-foil be moistened with *dilute* H_2SO_4 and then exposed to the air, $CuSO_4$ will be formed.

[‡] A portion of H_2SO_4, in its action on Cu, suffers more complete decomposition, for sulphur is deposited.

[§] HCl with excess of air dissolves Cu at ordinary temperatures; the weaker acids, such as the acetic, have no effect upon Cu unless assisted by the oxygen of the air; the copper under such circumstances rapidly combines with O, and a salt of the acid is formed.

NO is disengaged, but with a stronger acid N_2O_4 (nitric peroxide) is evolved, and if the action takes place at a higher temperature N is generally one of the gaseous substances set free.

299. *The oxides.*—PbO, Bi_2O_3, CuO, and CdO, may be formed either by exposing the metals to a red heat, in air or oxygen, or by igniting their hydrates, carbonates, or nitrates. HgO may be formed either by heating $Hg(NO_3)_2$ or by heating Hg in air at a temperature of 371° C. Ag_2O and Hg_2O may be obtained by adding to a solution of any of their soluble salts a solution of KHO or NaHO, and drying the precipitate with care. Ag_2O, Hg_2O, and PbO are perceptibly soluble in H_2O, the other oxides are not. Ag_2O, Hg_2O, and HgO are decomposed by heat alone, the other oxides are not, they are, however, reduced to the metallic state on being heated in a current of H, or by being ignited in contact with C, and PbO and Bi_2O_3 are reduced on being heated in an atmosphere of CO. The metals are obtained on fusing their oxides with KCy, potassic cyanate being formed. On being heated with an excess of S these oxides are converted into sulphides, SO_2 being evolved. Dry Cl converts them into chlorides, the conversion in the case of Ag_2O, Hg_2O, and HgO takes place without the aid of heat; PbO, suspended in H_2O, is converted by Cl into PbO_2 and $PbCl_2$, a similar reaction takes place with Br. Some of the other oxides are converted by Cl in the presence of a solution of KHO into higher oxides. They all form hydrates with the exception of Hg_2O. The hydrate of argentic oxide, when dried at a temperature above 60° C., is decomposed into Ag_2O and H_2O. The hydrates are formed by adding to the solution of these salts one of the alkalies in excess. The behaviour of these oxides with the volatile and fixed alkalies is given in Table VI. Ag_2O, Hg_2O, and CuO are black; HgO is black when hot, light red when cold; Bi_2O_3 is yellow, PbO is also yellow or reddish yellow; CdO is brown or yellowish brown; AgHO is brown, HgH_2O_2 is yellow, CuH_2O_2 is light blue, and PbH_2O_2, CdH_2O_2, and $Bi_2H_6O_6$ are white.

300. *The sulphides.*—The sulphides of this group are insolu-

ble in water, and dilute acids in the cold. Ag_2S, PbS, Bi_2S_3, CdS are also insoluble in the alkalies, alkaline sulphides, and KCy; Hg_2S and HgS are insoluble in solutions of the alkalies, ammonic sulphide, and KCy, but these sulphides dissolve in K_2S or Na_2S in the presence of NaHO or KHO, the solution in the case of Hg_2S being attended with a separation of Hg. CuS is insoluble in the caustic alkalies, and in the fixed alkaline sulphides it dissolves only to a very trifling extent, but it is a little more soluble in ammonic sulphide; it is soluble in a solution of KCy. They are all decomposed and dissolved with separation of sulphur in boiling HNO_3, with the exception of Hg_2S and HgS; these latter, and also the other sulphides, are decomposed and dissolved by *aqua regia*. *Out of contact with the air* Hg_2S is decomposed at a gentle heat into Hg and HgS, which sublimes without fusing or decomposing; Bi_2S_3 volatilizes at a red heat; PbS fuses at a red heat and volatilizes at a stronger heat without decomposing; CuS loses one half its S on being heated, and becomes converted in Cu_2S, which is not decomposed by heat alone. If heated in a current of air or O they are decomposed, Hg and Ag being left in the metallic state, the other metals are left as oxides; CuS in the moist state oxidizes on exposure to the air at ordinary temperatures. HgS, Ag_2S, PbS, Bi_2S_3 are reduced to the metallic state on being heated strongly in a current of H; Cu_2S is not reduced. Some of these sulphides, and probably all, undergo partial decomposition on being heated in a current of steam. On fusion with many metals, as Fe, Zn, Cu, Pb, Sn, Sb, &c., HgS and Ag_2S are decomposed, the added metal taking the S; PbS is deprived of its S by Fe, Zn, Cu, Sn, &c.; Cu_2S is not completely decomposed on fusing it with Fe, Sn, or Sb If Cu_2S* or Ag_2S is roasted with NaCl, CuCl or AgCl and Na_2SO_4 are formed. If a solution of $CuCl_2$ and NaCl is added to Ag_2S, AgCl and CuS are formed. PbO and CuO, mixed with their sulphides in equivalent proportions and heated, yield the metals and SO_2; and a mixture of their sulphates and sulphides in equivalent proportions, on being heated, likewise yields the metal and SO_2, thus:

---

* FeS_2 on being roasted with NaCl becomes converted into Fe_2Cl_6, Na_2SO_4 being formed.

$$PbS + PbSO_4 = 2Pb + 2SO_2$$

The colours of the sulphides, *when obtained by precipitation*, are given in the table, with the exception of those of Hg_2S and Ag_2S, which are black. They can be obtained in the dry way by heating together the metal and S with the exception of Hg_2S and CuS; their colour *when so obtained*, is the same as that of the native sulphides; the *artificial* or *native* Ag_2S is *blackish grey*, PbS and Bi_2S_3 are *lead grey*, the colour of CdS is the same as that of the precipitated sulphide; HgS exists both amorphous and crystalline, the crystalline sulphide in mass is of a cochineal colour and is called *cinnabar*, its powder is scarlet and is called *vermilion*; the amorphous sulphide is black, it is converted into the *red* both by sublimation and by the action of aqueous alkaline persulphides; the red is converted into the black by heating it moderately out of contact of the air.

301. *The chlorides.*—$CuCl_2$, $CdCl_2$, and $BiCl_3$ may be obtained by dissolving their oxides or carbonates in HCl; HgCl (calomel), AgCl, and $PbCl_2$ are best formed by adding to any of their soluble salts in solution HCl or an alkaline chloride in solution; $HgCl_2$ (corrosive sublimate) may be formed by dissolving HgO in boiling dilute HCl. In the dry way HgCl is formed by triturating equivalent proportions of Hg and $HgCl_2$ until the metallic globules disappear, and then subliming the mixture. $HgCl_2$ is formed by mixing intimately 2½ parts of $HgSO_4$ and 1 part of NaCl, and then subliming the mixture, and $BiCl_3$ may be formed by heating Bi in Cl, or by mixing Bi in fine powder with twice its weight of $HgCl_2$, and then distilling. HgCl and AgCl are insoluble, but the latter is soluble in strong solutions of NaCl. $PbCl_2$ is difficultly soluble, the other chlorides are soluble in water; $BiCl_3$ is decomposed by H_2O, BiOCl being formed, which is insoluble in H_2O, but soluble in diluted HCl. The chlorides of this group are not decomposed by heat alone; on being heated HgCl volatilizes

below a red heat and without first melting; $HgCl_2$, $BiCl_3$, and $CdCl_2$ fuse before volatilizing; the first of these boils at 295°, the other two volatilize at a moderate heat; AgCl volatilizes partially at a red heat; $PbCl_2$ not in contact with the air volatilizes at high temperatures, but in contact with air a portion volatilizes with excess of Cl, whilst a residue of PbO, $PbCl_2$ remains; $CuCl_2$ at a red heat loses half its Cl, CuCl remaining. They are all decomposed on being heated in a brisk current of hydrogen. They are all, with the exception of the mercury chlorides, decomposed when heated in a current of steam, the metal being left in the state of oxide, excepting in the case of bismuth and silver, the former of these being left as an oxychloride, the latter in the metallic state. With the exception of AgCl, HgCl, and $HgCl_2$, they are all converted into oxides on being heated in a current of O or of atmospheric air.

302. *The nitrates.*—The oxides and their hydrates are readily soluble in HNO_3, most of them form basic as well as neutral nitrates; the neutral nitrates are all soluble in water; $Pb(NO_3)_2$ and $Bi(NO_3)_3$ are, however, only sparingly soluble in H_2O; $HgNO_3$, $Hg(NO_3)_2$, $Bi(NO_3)_3$ are decomposed by H_2O, an insoluble, or sparingly soluble, salt being one of the substances formed. Freshly precipitated Ag_2O decomposes $Cu(NO_3)_2$ by boiling the oxide in a solution of that salt, CuO being precipitated, and $AgNO_3$ (lunar caustic) being formed.

303. *The sulphates.*—Bi_2O_3, CuO, CdO and their hydrates dissolve readily in diluted H_2SO_4. $HgSO_4$ is decomposed by H_2O into a sparingly soluble basic salt. $PbSO_4$ is insoluble in water, the sulphates of the other metals are soluble; Hg_2SO_4 is decomposed by H_2O, especially if hot, into a soluble acid and insoluble basic salt; under certain circumstances $Bi_2(SO_4)_3$ is decomposed by H_2O into an insoluble salt. $PbSO_4$ is not decomposed by heat alone, the other sulphates are; but Ag_2SO_4 is very difficultly reduced by heat, it is not decomposed by a red heat, bearing a much higher temperature than $CuSO_4$, $FeSO_4$, and Fe_23SO_4.

304. *The general characters of the salts of this group.*—The salts of Pb, Cd, and Bi are colourless if the acid be colourless;

the soluble silver salts are colourless, so are many of the mercury salts, but some of the basic mercuric salts are yellow; many of the silver salts acquire a violet tint, and ultimately turn black on exposure to light; the cupric salts in the anhydrous state are white, but in the hydrous state they are blue or greenish blue, which colour their solutions exhibit even when much diluted. The soluble *neutral* silver salts are *neutral*, but the soluble neutral salts of the other metals of the group are *acid*, to test-paper. The mercurous and mercuric salts volatilize when heated either with or without decomposition; the soluble neutral salts of Ag, Bi, Cd, and Cu are decomposed at a red heat; the plumbic salts sustain a red heat without alteration, unless the acid is very volatile or decomposable. The basic salts of Pb are alkaline to test-paper. Nearly all the silver salts are anhydrous. Ag and Hg are precipitated from the solutions of their soluble salts by many reducing agents, as SO_2, $FeSO_4$, and by the following metals:—Fe, Zn, As, Sb, Sn, Bi, Cu, Cd, Pb; and Hg also precipitates Ag. Fe, Zn, and other metals separate Ag from AgCl in the presence of H_2O. Hg, on being separated, frequently forms an amalgam with the metal; Bi is precipitated from its solutions by Zn, Fe, Sn, Cd, Pb, and Cu; Pb is thrown down by Zn, Cd, Sn, and slowly by Fe; Cu is precipitated by Zn, Fe, Cd, Sn, Pb; and Cd is precipitated from its solutions by Zn. $BaCO_3$ or $CaCO_3$ precipitates CuO, Hg_2O, HgO, Bi_2O_3, as hydrates from solutions of their salts by digesting them in the solution.

REMARKS ON THE INDIVIDUAL MEMBERS OF THIS GROUP, WITH ADDITIONAL SPECIAL TESTS.

305. Ag *and its compounds.*—Ag is the whitest of all metals; in the finely divided state, as obtained by the precipitation of metals, it is a dull dark grey powder. It is harder than Au, and softer than Cu. It melts at a white heat. Its conductivity for electricity and heat is greater than that of any other metal; its conductivity decreases with the temperature. It combines with Cl, Br, I, at ordinary temperatures, and readily

with S, P, and As. It undergoes no change when heated in contact with melted alkaline nitrates or with the hydrates of the alkalies; crucibles of silver are, therefore, very useful when these substances have to be fused, as Pt is acted upon by them in their fused state. The affinity of Ag_2O for acids is greater than that of CuO and ZnO. Ag_2O is insoluble in the fixed alkalies, but readily soluble in NH_4HO, with which it combines, giving rise to a dangerous compound (fulminating silver), the composition of which has not been ascertained with certainty; by some it is supposed to be a compound of Ag_2O and NH_3, by others an amide or nitride of silver. AgCl, when strongly heated, melts, and on cooling has the appearance of *horn*, from which circumstance it has been named *horn silver*. If recently precipitated and still moist AgCl is boiled with excess of KHO, it is converted into Ag_2O. By the action of light argentic salts turn black, and are readily decomposed, Ag being separated; if any oxidizable matter is present, and even when no organic matter is present, many of them acquire a violet tint, and ultimately turn black. Silver forms the best surface for reflectors by reason of its superior power for reflecting light. Pure silver is unfitted for the manufacture of coins or other articles intended for useful purposes, owing to its softness; it is, therefore, alloyed with a small quantity of Cu, which increases its hardness without affecting its colour much; the proportion of Cu in the 'standard' silver employed for coinage varies in different countries; in England it amounts to 7·5 per cent., and in France to 10 per cent. Silver solder is an alloy of Ag, Cu, and Zn, containing about 66 per cent. of Ag.

306. The principal minerals of this metal are the SULPHIDE (*silver glance*, Ag_2S), the CHLORIDE (*horn silver*, AgCl), SULPHIDE OF SILVER and ARSENIC ($3Ag_2S + As_2S_3$), and SULPHIDE OF SILVER and ANTIMONY ($3Ag_2S + Sb_2S_3$); SILVER is also met with in the metallic state. It is likewise found in small quantities in most lead and copper ores.

307. When silver compounds, mixed with *carbonate of soda*, are subjected on charcoal to the inner blowpipe flame, brilliant

metallic globules are produced, which are not attended with any incrustation.

308. "If silver occurs only in traces in slags or complex ores, it can only be detected by the well-known method of cupellation. If, however, the silver compound is not mixed with a very large amount of foreign matter, it can be detected in very minute quantities by reduction with soda on the charcoal splinter. The white ductile beads dissolve easily on warming in dilute HNO_3, and yield AgCl with HCl, which can then readily be recognised by its behaviour with HNO_3 and NH_4HO. Less than one tenth of a milligramme of silver can thus be easily detected with certainty."—*Bunsen.*

Characteristic reactions.—That with HCl and the solubility of the AgCl in NH_4HO.

309. Ag forms at least one other oxide, the neutral peroxide, Ag_2O_2, which is formed by decomposing by the voltaic current a weak solution of $AgNO_3$; there is also some reason to believe in the existence of a suboxide, Ag_4O. Both these oxides, if the latter exists, are decomposed by acids, argentic salts being formed.

310. Hg *and its compounds.*—Hg is the only metal that is fluid at common temperatures. It freezes at —39°, and boils at 350° C. It enters into combination with Cl and Br at ordinary temperatures. It combines with I and S in the cold, if triturated with them. HI and H_2S are slowly decomposed by it, H being evolved. It combines with most of the metals at ordinary temperatures, forming alloys which are termed amalgams. Hg_2O is so unstable that it is decomposed even when dry on exposure to diffuse daylight into HgO and Hg. HgO is obtained in the form of red scales by the ignition of $Hg(NO_3)_2$, and in the form of a bright yellow powder by adding KHO to solutions of mercuric salts. When the scales are heated they become nearly black, but on cooling the red colour returns. HgO forms a soluble compound with BaO. $H_2C_2O_4$ combines with the yellow oxide in the cold, but does not act on the red oxide; an alcoholic solution of $HgCl_2$ converts the yellow oxide into the black oxychloride, but it does not act on

the red oxide. When NH_4HO is added to the yellow oxide a yellowish-white amorphous powder is produced, which is the hydrate of a powerful base, mercuramine ($Hg_4H_4N_2O_3$, $3H_2O$). The precipitate produced by K_2CO_3 in solutions of $HgCl_2$ is the yellow oxide; that by $KHCO_3$ is the red oxychloride.

311. The fixed alkalies, like NH_4HO, change HgCl into a *black* compound; but the compound produced by the action of the fixed alkalies on HgCl is Hg_2O, whilst the compound produced by NH_4HO is, as is shown in the table, dimercurous-ammonic chloride. The following is the reaction:—$2HgCl + 2NH_4HO = Hg_2H_2NCl + NH_4Cl + 2H_2O$. NH_3 is absorbed by HgCl, mercurous-ammonic chloride being formed, thus:—$HgCl + NH_3 = HgH_3NCl$.

312. NH_4HO, added in *excess* to a solution of $HgCl_2$, produces a white precipitate of dimercuric diammonic dichloride ($Hg_2H_4N_2Cl_2$). This substance is used in medicine under the name '*white precipitate.*' The action of NH_4HO on the two mercury chlorides is very analogous. The following is the reaction on $HgCl_2$:

$$2HgCl_2 + 4NH_4HO = Hg_2H_4N_2Cl_2 + 2NH_4Cl + 4H_2O.$$

If on the addition of NH_4HO to the $HgCl_2$ solution the latter is maintained in considerable *excess*, the precipitate has a different composition to what it has in the preceding case. The *empirical* formula of the precipitate in this latter case is $Hg_4H_4N_2Cl_6$; its *rational* formula may be $Hg_2H_4N_2Cl_2 + 2HgCl_2$, a double salt, composed of one equivalent of dimercuric diammonic dichloride and two equivalents of mercuric chloride.

313. For the action of soluble iodides on mercurous and mercuric salts see pars. 478 and 479.

314. The presence of Hg may be detected in solution by placing in it a small strip of Zn, round which a thin strip of gold foil is twisted. The Hg will be deposited on the Au by voltaic action in the form of a *white stain*, which disappears on heating the Au to redness.

315. Cu, introduced into a solution of a mercurous or a mercuric salt, especially after adding HCl, becomes covered

with a white lustrous coating; when moderately heated, the Cu regains its original colour, vapours of Hg being evolved: this test is exceedingly delicate. Slips of copper wire, about an inch in length, may be used; they should be cleaned by shaking for a few moments with concentrated HNO_3, and thoroughly washed. Half a dozen such slips should be boiled for three or four minutes in the solution, previously acidulated with HCl; they are then well rinsed, dried by pressure between blotting-paper, and heated in a glass tube of one quarter of an inch diameter, constructed so as to allow the passage of a feeble current of air. A coating of minute *globules of* Hg is formed upon the cool part of the tube; these may be united into larger globules by rubbing with a glass rod. The copper wire being removed, a very minute particle of I may be introduced into the tube, and a gentle heat applied to vaporize it. The sublimate of Hg will thus be converted into HgI_2, which is yellow at first, and becomes scarlet when rubbed with a glass rod.

316. If $SnCl_2$ be added in small quantity to mercuric salts, it reduces them to mercurous salts, and, as a consequence, HgCl precipitates; but if it be added in excess, the mercury salt (mercurous as well as mercuric) is completely decomposed, Hg being thrown down as a grey precipitate, which may be united into globules by heat and agitation—but most readily by boiling the metallic deposit, after decantation of the supernatant fluid, with HCl.

317. *Detection of* Hg *in organic liquids.*—Acidify with a few drops of HCl; add a few strips of copper wire or foil, and boil for about half an hour; then remove the Cu from the liquid and wash it with a little dilute solution of NH_4HO, so as to remove any copper oxide; then dry it by gentle pressure between folds of bibulous paper, and examine it according to par. 315.

318. *Detection of* Hg *in organic solids.*—The solid cut into small pieces is heated with HCl and $KClO_3$, as directed in par. 733; after being boiled for a few minutes, it must, after cooling, be filtered, and the filtrate evaporated to a small bulk;

if any solid separates during the evaporation, it is again filtered, washed H_2S is passed through the concentrated fluid; if a black precipitate is formed, it must be collected upon a filter, and washed with H_2O until all Cl is removed, and then purified by boiling it in dilute HNO_3; it is afterwards dissolved in as small a quantity of aqua regia as possible, and examined for Hg according to par. 296—2nd.

319. Solid compounds of Hg, mixed with a large excess (at least twelve parts) of *dry* Na_2CO_3, and heated in a perfectly, dry tube of hard glass, having a diameter of about one quarter of an inch, and expanded into a bulb at one end, furnish minute *globules*, Hg, which are deposited on the cool part of the tube and may be united into larger globules by rubbing with a glass rod. This test is exceedingly delicate; in order that it may be perfectly successful, the Hg compound should be thoroughly dried (in a water-bath), and the Na_2CO_3 should be ignited immediately previous to use. In order to prevent the sublimation of undecomposed Hg compounds, it is well to cover the mixture in the bulb-tube with a layer of pure Na_2CO_3.

320. The chief mineral of this metal is the MERCURIC SULPHIDE (*cinnabar*); it is likewise met with in the metallic state.

321. *Flame reactions.*—(*a*) *Metallic film* is mouse-grey, non-coherent, and spreads over the whole basin. To obtain small traces of Hg in the reduced state, the sample is mixed with soda and KNO_3, and filled into a thin test-tube five to six millims. wide and ten to twenty millims. long. This is held by a Pt wire in the flame, whilst the bottom of the basin, filled with cold water, is placed close above the open end of the tube. If the quantity of Hg is considerable, it collects in the form of globules, which can be seen with a lens, and which can be collected into larger drops by wiping the basin with a piece of moistened filter-paper.

(*c*) *Iodide-film* is obtained by breathing on the metallic film, and then placing it over the vessel (fig. 8 of the *Plate*) containing moist Br. It first becomes black, and then disappears, but not until after some time; $HgBr_2$ is formed. If the basin be now placed above the vessel of fuming HI, a very characteristic carmine-coloured film of HgI_2 is produced; this is often accompanied by HgI, but neither of these disappears on breathing, nor when blown with ammonic air.

(*d*) *Sulphide-film* black, not altered by breathing or by blowing with $(NH_4)_2S$.—*Bunsen.*

Characteristic reactions.—For mercurous compounds those with HCl and NH_4HO. For mercuric compounds those with KI, NH_4HO, and KHO.

322. No other oxides of Hg are known.

323. Bi *and its compounds.*—The colour of Bi is reddish-white; it is hard and brittle, and when pure crystallizes more readily than any other metal. It melts at 264° C., and it volatilizes at high temperatures. If projected into an atmosphere of Cl it takes fire; it also unites readily with I, Br, and S. Bi_2O_3 melts at a red heat; *it* and the *hydrate* are both readily soluble in dilute mineral acids. The hydrate is dehydrated on boiling it in solutions of KHO. Many of the bismuthic salts crystallize well, but they cannot exist in solution unless an excess of acid is present, as they are decomposed by water, and this is one of their distinguishing characters, into insoluble basic and soluble acid salts; this property is exhibited in the most decided manner by the chloride. Bi is found principally in the metallic state. Pewter and Britannia metal are alloys of Cu, Sn, Sb, and Bi. Newton's fusible metal and the metal for calico-printing blocks are alloys of Sn, Pb, and Bi.

324. The decomposition of the chloride by H_2O is employed as a confirmatory test for Bi. The precipitate produced by NH_4HO is dissolved in a small quantity of HCl, evaporated to all but dryness, and is then poured into a large quantity of water; when Bi is present, a milky turbidness will be produced.

325. K_2CrO_4 throws down from solution of Bi the YELLOW CHROMATE. $Bi_2(CrO_4)_3$ differs from $PbCrO_4$ by its solubility in dilute HNO_3, and its insolubility in KHO.

326. For detecting Bi in the presence of Pb, see par. 337.

327. When bismuth compounds mixed with Na_2CO_3 are exposed on charcoal to the inner blowpipe flame, brittle metallic globules are obtained, attended with a yellow incrustation of Bi_2O_3.

328. *Flame reactions.*—(*b*) *Reduction-film* black, dead or brilliant; thin portion of film brownish black.

(*c*) *Oxide-film* light yellow; unaltered by $AgNO_3$ with or without ammonia; gives no reaction with $SnCl_2$, but yields black precipitate of Bi_2O_2 on addition of NaHO.

(*d*) *Iodide-film* is very characteristic, and remarkable for the number of tints which it assumes. The thick part is of a brown or blackish-brown colour, with a shade of lavender blue; the thin film varies from flesh colour to light pink; it easily disappears on breathing, and appears again on blowing. In a stream of ammonic air it passes from pink to orange, and on blowing or warming it again attains a chestnut-brown colour; it resembles the oxide-film in its behaviour with $SnCl_2$ and NaHO.

(*e*) *Sulphide-film* is of a burnt umber colour; the thin parts are of a lighter coffee-brown colour, does not disappear on blowing, and is not soluble in $(NH_4)_2S$.

(*f*) *On charcoal splinter with soda* the bismuth compounds are reduced to a metallic bead, yielding, when rubbed in the mortar, bright shining yellowish splinters of metal soluble in HNO_3. The solution gives, with $SnCl_2$ and NaHO, black Bi_2O_2.

Characteristic.—The decomposition of the chloride by water, the reaction with K_2CrO_4, and the flame reactions.

329. Three other oxides of Bi are known, viz. bismuthic anhydride (Bi_2O_5), also Bi_2O_4, which may be regarded as a compound of Bi_2O_3 and Bi_2O_5, and a dioxide, Bi_2O_2. The first of these oxides is obtained by passing Cl into a strong solution of KHO, in which is suspended bismuthous hydrate; a blood-red solution of potassic bismuthate and a red precipitate is formed. The red precipitate is digested in HNO_3 to remove the bismuthous oxide, with which it is always mixed; a red

powder is left, which is bismuthic acid, $HBiO_3$. By a heat of 270° it is rendered anhydrous, and assumes a brown colour. At a somewhat higher temperature it loses oxygen, and becomes converted into the second oxide, Bi_2O_4. Bi_2O_2 is obtained by treating equivalent quantities of $BiCl_3$ and $SnCl_2$ with an excess of KHO, filtering and drying in an atmosphere of CO; it is black in colour, and takes fire when heated in the air, being converted into Bi_2O_3.

330. Cd *and its compounds.*—This metal is of a white colour; it is soft, it melts below a red heat; it is more volatile than Zn, and it volatilizes somewhat below the boiling-point of Hg. CdO is quite fixed in the fire, and does not melt at the strongest white heat. CdO and its hydrate are both easily soluble in dilute mineral acids; most of the salts of Cd are soluble in water. Cd occurs only in zinc ores. It is found as sulphide in zinc blende, and as oxide or carbonate in calamine.

331. When compounds of Cd, mixed with Na_2CO_3 or other reducing agents, are exposed on charcoal to the inner blowpipe flame, the charcoal becomes covered with a yellow or reddish-yellow incrustation of CdO.

332. *Flame reactions.*—(*a*) *Metallic-film* black; the thin parts brown.

(*b*) *Oxide-film* brownish-black, shading off through brown to a white invisible film of suboxide, which is not altered by stannous chloride, either alone or with soda; $AgNO_3$ produces a blackish-blue coloration of reduced metal, which is very characteristic and does not disappear on addition of NH_4HO.

(*c*) *Iodide-film* white, no change produced by NH_4HO.

(*d*) *Sulphide-film* lemon-yellow, insoluble in ammonia.

(*e*) *Reduction on charcoal splinter with soda.*—The metal, owing to its volatility, can only with difficulty be obtained as a silver-white ductile bead.

Characteristic reactions.—The colour of the sulphide and the flame reactions.

333. Cd forms another oxide, Cd_2O; it is obtained by heating CdC_2O_4; it is a green powder, and is decomposed by heat or acids into Cd and CdO.

334. Pb *and its compounds*.—Pb is of a bluish-white colour; when cut, the fresh surfaces have considerable lustre; it is very soft, malleable, and ductile; it leaves a streak upon paper; it fuses completely at 335° C., and at a red heat gives off vapours. It combines directly with S, P, and As, and alloys with most of the metals. The chief of the useful alloys of which this metal is a constituent have already been noticed. It is readily oxidized by CuO, which is reduced to the state of Cu_2O. PbO in commerce frequently goes under the name of *massicot*, and when partially fused is called *litharge*. PbO melts readily at a low red heat, and dissolves glass and earthenware, forming readily fusible silicates. It has a considerable affinity for acids; the best solvent both for it and the hydrate is HNO_3 or acetic acid; the hydrate speedily absorbs CO_2 from the air. Oxide of lead dissolves in 7000 parts of pure water; its *solubility* is greatly diminished in the presence of certain salts, sulphates, phosphates,* and carbonates for example, and *increased* by NH_4HO and its salts. Metallic lead undergoes no change when sealed up in pure water, from which the air has been expelled by boiling. It is oxidized, however, when exposed to the influence both of air and water; the oxide thus formed dissolves in the water, and this solution absorbs CO_2 from the air; a film of hydrated carbonate of lead, PbH_2O_2 $PbCO_3$, is thus formed which is deposited in silky scales. Another portion of oxide becomes formed on the surface of the metal, which is also dissolved by the water, and thus a rapid solution of the metal ensues. This action is materially modified when certain salts exist in the water, even when they do not exceed three or four grains in the gallon. The solvent action is *increased* by the presence of chlorides and nitrates, but is diminished when sulphates, phosphates, or carbonates are present, the PbO being scarcely soluble in water containing these latter salts. Acid carbonate of lime is remarkable for its preservative influence, and in consequence of the presence of this salt in most

---

* Dr. Frankland has recently observed that water which dissolves lead ceases to do so after it has been passed through animal charcoal, by reason of its having dissolved some of the phosphate of lime in the charcoal.

spring water these waters do not act on lead to any serious extent, a film of carbonate of lead being deposited on the surface of the metal and protecting it from further action. The presence of nitrogenous organic matter in water is dangerous, as nitric acid may be formed by its oxidation. As lead is so constantly employed in making cisterns, pipes, &c., for domestic purposes, the action of water on this metal is very important in a sanitary point of view.

335. The principal minerals of this metal are the SULPHIDE (*galena* or *lead glance*, PbS) and the CARBONATE ($PbCO_3$).

336. K_2CrO_4 produces, in solutions of Pb, a yellow precipitate of $PbCrO_4$, insoluble in HNO_3, but soluble in the fixed alkalies, from which solutions $PbCrO_4$ is precipitated on adding acetic acid in excess.

337. When KI is added to a solution of a salt of Pb, yellow PbI_2 is precipitated, which dissolves on heating the liquid, and is re-precipitated on cooling in *brilliant golden-coloured scales.*[*] The solution of the amorphous iodide may be greatly facilitated by the addition of a small quantity of HCl. If the *least trace of* Bi is present in the lead salt, the re-reprecipitated scales are *no longer yellow*, but assume a *dark orange* or *crimson* tint, varying in intensity of colour according to the amount of Bi present. This test for Bi is of extraordinary delicacy.

338. *Detection of* Pb *in waters.*—Place two beakers on white paper, side by side; pour into each a pint of the water to be examined; add a little pure HCl to the water in one of the beakers, and subsequently some H_2S; if, after the addition of the H_2S, the water becomes browner in colour than the water to which no H_2S has been added, lead is indicated; by this method a quarter grain of lead in a gallon of water can be detected. As organic matter interferes with the reaction, it is necessary to evaporate the water, if it contains much organic

---

[*] PbI_2 is very soluble in solutions of the acetates of soda, potash, and ammonia, even in the cold forming colourless solutions, from which KI, added in excess, precipitates PbI_2 in the crystalline state, although no heat has been applied.

matter, to dryness with a few drops of HNO_3, and ignite the residue; to the residue afterwards should be added some $HC_2H_3O_2$ and water, and the mixture heated, and, if necessary, filtered, and to the filtered or unfiltered liquid H_2S should be applied.

339. *Detection of* Pb *in organic mixtures.—If the mixture is in the liquid state,* a little HNO_3 is added, and the mixture must be then filtered, and washed H_2S passed through the filtered liquid to excess; a dark-coloured precipitate will be formed if lead is present. When a dark-coloured precipitate is formed, it is allowed to subside, it is then collected on a filter, and after being thoroughly washed with water, it is dissolved in HNO_3, and the solution tested for lead according to 336.

340. *If the mixture is in the solid form,* it may either be heated with HCl and $KClO_3$, as described at par. 733, or it may be dried, and the dried mass heated to dull redness until the ash is of a grey colour; it is then dissolved in dilute HNO_3, and treated with H_2S, &c., as in the preceding case.

341. When lead compounds, mixed with Na_2CO_3, are exposed upon charcoal to the inner blowpipe flame, ductile metallic globules are formed, accompanied with an incrustation which is yellow whilst hot, but becomes paler on cooling.

342. *Flame reactions of plumbic compounds.—(a) They colour the flame pale blue.*

(*b*) *Reduction film* black, dead or brilliant.

(*c*) *Oxide-film* bright yellow-ochre-coloured; stannous chloride gives no reaction even on addition of NaHO; $AgNO_3$ does not produce any reaction, either alone or on addition of NH_4HO.

(*d*) *Iodide-film* orange- to lemon-yellow, insoluble on breathing or on moistening; disappears on blowing with ammoniacal air, and again appears on warming.

(*e*) *Sulphide-film* brownish-red to black; by blowing or moistening with $(NH_4)_2S$ it remains unaltered.

(*f*) *On charcoal splinter with soda* gives a grey, very soft, ductile metallic bead, which is slowly but completely soluble in HNO_3, yielding a white easily crystallizable salt, soluble in

H_2O, and precipitated as a white powder on addition of H_2SO_4 from a capillary tube.

Characteristic reactions.—Those with H_2SO_4, HCl, K_2CrO_4, and H_2S.

343. Although PbO is the only lead oxide which forms salts with acids, three other oxides are known, viz. Pb_2O (black suboxide), PbO_2 (binoxide), and red lead, which is a compound of the two oxides, PbO_2 and PbO; its composition varies, but 2PbO, PbO_2 represents an average composition. Pb_2O is obtained by heating PbC_2O_4 cautiously in a retort, from which air is excluded; it is converted with acids into plumbic salts. Red lead is obtained by keeping PbO, at a dull-red heat, in contact with the air for a considerable time; it is decomposed at a red heat into PbO and O; HNO_3 decomposes it, dissolving out PbO, and leaving PbO_2. PbO_2, sometimes called puce oxide, is a brownish-black substance; it may be obtained, as we have noticed, by treating red lead with HNO_3; it may be prepared in many other ways—it may be obtained, for instance, by adding to PbO or $Pb\bar{A}$, in the presence of water, Cl or CaOCl; it is decomposed by heat into PbO and O; SO_2 converts it into $PbSO_4$; it is often employed in the laboratory to absorb SO_2; H_2SO_3 converts it into $PbSO_4$, thus:

$$PbO_2 + H_2SO_3 = PbSO_4 + H_2O;$$

treated with concentrated HCl in the cold, or heated with dilute HCl, it is converted into $PbCl_2$, thus:—

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

344. Cu *and its compounds.*—This metal is of a red colour. In the finely divided state it is a soft, dark red, dull-looking powder. If exposed to a very intense heat it volatilizes, but it is usually considered fixed in the fire. It is an excellent conductor of heat and electricity, standing in this respect next to Ag. In the state of foil or filings it takes fire in an atmosphere of Cl. At ordinary temperatures, and at a *red* heat, it unites directly with Br, I, S, Si, &c. Concentrated HI dissolves it readily, H_2 being evolved. The fixed alkalies

have little or no action on it, but NH_4HO gradually dissolves it if exposed to the air; the compound in solution, which is of a deep blue colour, has the formula $CuO(NH_3)_2$; a nitrate is formed at the same time. Cu, introduced into a gas or alcoholic flame, communicates to it a *green colour*. CuO and its hydrates dissolve with facility in the mineral acids, even in their diluted state. If CuO is gently ignited with Cu, there is formed Cu_2O: When CuO is boiled with $SnCl_2$, SnO_2 is precipitated, and CuCl dissolved. With P at a red heat, CuO yields phosphide and phosphate of copper. CuO appears to unite with ammonia in more than one proportion. When NH_4HO is not added in excess to cupric salts, a basic cupric salt, free from ammonia, is usually precipitated. NH_4HO added to $CuSO_4$ produces at first a basic cupric sulphate, which dissolves on the addition of more NH_4HO, forming a deep blue solution, which may be considered as containing ammonic sulphate in combination with ammonic cuprate, having the following formula:—$(NH_3)_4Cu$. Cu is a constituent of many useful alloys, the chief of which have been already noticed under the heads of the other metals. If bright metallic iron be introduced into copper solutions, it becomes coated with a red deposit of that metal, provided the solution be neutral or only very slightly acid.

345. This metal is sometimes found in the native state, but it chiefly occurs in combination with iron sulphide, constituting the COPPER PYRITES ($Cu_2S + Fe_2S_3$), and in BLUE COPPER ore, or MALACHITE ($CuCO_3$, CuO, H_2O).

346. $K_4Fe''Cy_6$ throws down, even from dilute solutions of copper, a reddish-brown precipitate of $Cu_2Fe''Cy_6$, which is insoluble in dilute acids, is decomposed by the fixed alkalies, is soluble in NH_4HO, which solution has a deep blue colour.

347. *Detection of copper in organic liquids.*—Acidulate with HCl, introduce a piece of polished iron (344), and allow it to remain in the liquid several hours if no perceptible deposition takes place in a shorter time. If any doubt exists about the deposit, examine either a portion of the solution which has not

had the iron test applied to it, or by dissolving some of the precipitate, which has been scraped off the iron, in HNO_3, and examining that or the original solution with NH_4HO or $K_4Fe''Cy_6$.

348. *Detection in organic solids.*—The substance to be examined is cut into small pieces, and treated with HCl and $KClO_3$, as directed at par. 733. The acid solution, after filtering it, is evaporated nearly to dryness, and then examined by one or other or by all the following tests:—Fe (par. 344), NH_4HO (Table VI, W 3), $K_4Fe''Cy_6$ (par. 346).

349. When any copper compounds, mixed with Na_2CO_3, are exposed on a charcoal support to the inner blowpipe flame, Cu is obtained, unaccompanied with any incrustation on the charcoal.

350. *Flame reactions.*—(*a*) *On the charcoal splinter with soda* the copper compounds yield a ductile lustrous metallic bead, easily recognisable by its red copper colour. By rubbing in the mortar, flat metallic particles are obtained, which can be readily washed, and are easily soluble in HNO_3. The blue solution, absorbed on filter-paper, yields a brown stain on addition of $K_4Fe''Cy_6$. Instead of acting upon the metal in a curved glass, it may be dissolved by moistening paper upon which it is placed with HNO_3.

(*b*) *With borax on platinum wire.*—Blue bead, not altered to cuprous oxide when heated in the lower reducing flame alone, but on addition of very little tin-salt forms a reddish-brown bead. If this bead be frequently oxidized and reduced in the flame, a ruby-red transparent bead is obtained; this occurs most readily when the bead is allowed to oxidize very slowly.—*Bunsen.*

Characteristic reactions.—Those with NH_4HO and K_4FeCy_6.

351. Three other oxides of copper are known, viz. Cu_2O, Cu_4O, and Cu_2O_3; there is very little known about the last two. We have already noticed the formation of the first oxide, Cu_2O (par. 257), and we shall learn hereafter some other methods for its formation; it is of a red colour, and its solution in HCl absorbs O rapidly, and becomes converted into a cupric salt.

One of the most remarkable properties of the solutions of this oxide in HCl is that of absorbing CO, and forming with it a crystalline compound.

352. The following methods have also been proposed for the *separation* of Cd and Cu:

1st Method.—Acidify the solution, if it is not acid, with HCl; then pass H_2S through the solution. The two metals, if present, will be precipitated as sulphides; the precipitate must be well washed, and then boiled with dilute H_2SO_4. The CdS is decomposed by the H_2SO_4, $CdSO_4$ being formed, which dissolves, whilst the CuS is undecomposed and undissolved. Separate the two by filtration, test the filtrate for Cd by H_2S; dissolve the CuS in HNO_3; neutralize with NH_4HO, acidify with acetic acid, then add $K_4Fe''Cy_6$. This is a good method; the only precaution to be attended to is, that the mixed sulphides must be washed rapidly, so that the CuS may not become oxidized by exposure to the air.—*Dr. A. W. Hoffmann.*

2nd Method.—To one portion of the acetic solution add H_2S in excess. The formation of a yellow precipitate denotes Cd. If, on account of the presence of Cu, the CdS cannot be distinctly recognised, allow the precipitate produced by the H_2S to subside, decant the supernatant fluid, and add to the precipitate a solution of KCy until the CuS is dissolved. If a yellow residue is left undissolved, Cd is present; in the contrary case, not.—*Fresenius.*

353. Answers to the following exercises must be written out.

EXERCISES.

114. If after dissolving the precipitated sulphides of the second division of the sixth group in HNO_3, you were to add NH_4HO without first adding H_2SO_4, how would you examine the precipitate for Bi and Pb? Describe as many methods as possible.

115. I have some ferrous sulphate which contains some cupric sulphate: how must I precipitate the Cu, so that after the precipitation the ferrous sulphate remains perfectly pure?

116. How would you prepare pure argentic nitrate from an alloy of copper and silver?

117. What substances *increase*, and what substances *decrease*, the solvent action of water on lead?

118. What is the action of KHO on cupric salts, and how is this action modified in the presence of As_2O_3?

119. How would you proceed to detect and separate all the members of the sixth group, if you were to precipitate the members of the first as well as those of the second division with H_2S?

120. A mixture of PbS and $PbSO_4$, in the proportion of one equivalent of PbS to three of $PbSO_4$, is heated to near the fusing point: what changes take place?

121. Describe the processes for the detection of copper in mixtures containing organic matter.

122. Give the formula of the different lead oxides, and state how they are prepared.

123. A colourless solution is given you which you have to examine for the members of the six groups. What members must be absent?

124. Give the composition of the oxides and chlorides of mercury, and describe by equations the action of the volatile and fixed alkalies upon them; and state how mercurous and mercuric compounds are distinguished from each other.

125. The salts of another metal form, like the cupric salts, a blue solution with NH_4HO: name the metal, and state how you would distinguish the Cu and this metal from each other in a solution.

126. How would you detect corrosive sublimate in organic mixtures?

127. Give several methods of reducing AgCl.

128. The water in copper mines contains Cu and Fe in solution as sulphates, owing to the oxidation of some of the copper ore, Cu_2S, Fe_2S_3; the water is pumped into wood spouts, the bottoms of which are covered with pieces of scrap iron. What is the object of passing the mine-water over the iron?

129. Some red silver ore, $3Ag_2S$, Sb_2S_3, is placed in the bulb

of a glass tube; a stream of dry H is passed over it, and it is heated to fusion by means of a lamp; when pure H only escapes from the glass-tube the lamp is removed. What change has the H effected? Dry Cl is afterwards passed through the tube, and a gentle heat applied to the bulb: what change does the Cl effect, and what substance finally remains in the tube?

130. I have in solution arsenious and arsenic acids, and Cu, Ni, Co, and Fe in the ferric state. I diffuse $CaCO_3$ through the solution without heating it, and allow it to stand for some time. I then filter off and pass Cl through the filtrate, and again add $CaCO_3$. I again filter, and to the filtrate add lime-water. What change does the $CaCO_3$ effect, for what purpose is the Cl added, and of what does the precipitate consist which is produced by lime-water, and why is lime-water added in preference to KHO or NaHO?

131. An ore containing CuS, FeS_2, and Ag_2S, is roasted in contact with the air, the heat being gradually raised during the space of three or four hours to a dull-red, and finally to a bright-red; the roasted mass is finally heated with water, and metallic copper is introduced into the solution. What changes do the sulphides undergo in the first stages of the roasting, in what state are the metals finally left, and what substances remain undissolved, and what are dissolved by the water, and for what purpose is the Cu introduced into the aqueous solution.

132. Different processes have been proposed, and are carried out in the smelting of the sulphur ores of silver; sometimes the Ag_2S is fused with Pb; sometimes it is fused with $PbSO_4$, in equivalent proportions; sometimes it is fused with PbO in the proportion of an equivalent of the Ag_2S to two equivalents of PbO. Show by diagrams the reactions which take place in each case.

133. There is present in solution in HCl, Fe_2Cl_6, $CuCl_2$, $CoCl_2$, $NiCl_2$, and H_3AsO_4. I nearly neutralize the solution with Na_2CO_3. I then add sodic acetate in excess, and boil for some time, and afterwards filter. The filtrate I acidulate with

HCl, and then pass H_2S through it to excess, and again filter. I boil the filtrate to expel the excess of H_2S, and then pass Cl through it to excess, and then diffuse $CaCO_3$ through the liquid and allow it to stand for several hours. I afterwards add to the filtrate lime-water. What changes take place on boiling the solution after the addition of the alkaline acetate? What is precipitated by the H_2S, by the $CaCO_3$, and by the lime-water?

134. A silver ore containing Ag_2S, CuS, Fe_2S_3, NiAs, and $CoAs_2$, after being reduced to powder, is mixed with a tenth of its weight of NaCl; the mixture is afterwards roasted for several hours; when the roasting is complete the ore is raked out and allowed to cool; it is then sifted to separate the fully roasted portion, which is in fine powder, from the imperfectly roasted portion, which is in lumps; the fine powder, along with about a tenth of its weight of scrap iron, is introduced into casks about half filled with water; the casks are then made to revolve for about two hours; about half its weight of mercury is then introduced into the casks, which are then revolved for about twenty hours. The amalgam and mercury in excess are then separated from the spent material by washing, and the amalgam is afterwards separated from the mercury by filtration; the amalgam is finally placed on trays supported on a tripod, over which is placed a large bell-shaped iron vessel, the bottom of which rests in a vessel into which water is constantly flowing; round the upper part of the bell a fire is lighted, which brings that part of the bell and its contents to a red heat. What change do the metals undergo in roasting? What change do the iron and mercury effect? And what is the object of placing the amalgam under the iron vessel?

THE GENERAL PROPERTIES OF THE DIFFERENT BASIC GROUPS.

354. It will be seen by consulting Table VII, that some of the group-reagents precipitate more than one of the groups; the analysis must therefore be commenced by removing *the group* whose reagent does not precipitate the members of any

of the other groups under the same circumstances. Such a course will be adopted, if the reagents are employed in the order observed in the table.

355. FIRST DIVISION OF THE SIXTH GROUP.—The analysis must be commenced by adding to the solution HCl, which precipitates the 1st section of the 6th group if present. When a precipitate is produced, collect it upon a filter, wash it twice with cold water, and then examine it, according to the 1st section of Table VI, and par. 293. The wash-water must be collected with the filtrate. *Before adding the* HCl, *consult* pars. 376, 377, and 378.

356. The filtrate from the precipitate produced by HCl, or the solution with which that *acid* has failed to give a precipitate, must be examined for *the 2nd division of the 6th and the whole of the 5th group*, in the manner described in the next paragraph.

357. SECOND DIVISION OF THE SIXTH AND THE WHOLE OF THE FIFTH GROUP.*—H_2S† must be passed through the solution until it *smells strongly* of H_2S after it has been shaken and gently warmed for some time; the 2nd section of the 6th,

---

* Au and Pt are easily detected in the presence of all the metals (paragraph 331); Northcote and Church, in their 'Manual of Analysis,' recommend their separation from the solution, before precipitating the other members of the fifth and the members of the sixth group by H_2S; the following is their plan:—The filtrate from the HCl precipitate, or the solution which has failed to give a precipitate, is freed from HNO_3 (if present) by one or two evaporations on the water-bath with HCl; to the HCl solution, which ought to be concentrated, a reasonable quantity of NH_4Cl solution is added, the liquid is then well agitated and allowed to rest for some hours; if Pt is present, a yellow crystalline precipitate of $2NH_4Cl, PtCl_4$ is formed. The filtrate is mixed with a reasonable quantity of a concentrated solution of $H_2C_2O_4$, and moderately heated for some hours. A precipitate, consisting of yellow spangles or of a brown-yellow sponge indicates Au. The filtrate is then treated with H_2S.

† If the Ag_2O, PbO, and Hg_2O, had not to be sought for, we must nevertheless add HCl to the solution to render it acid, before adding H_2S, in order to prevent the members of the 3rd and 4th groups from being precipitated by that reagent, and to ensure the complete precipitation of the fifth group.

and the 5th group, when present, will be precipitated. When a precipitate is produced, collect it upon a filter and wash it with hot water, until the wash-water is no longer acid to test-paper; the wash-water need not be collected with the filtrate, but may be thrown away.

358. If the FIFTH GROUP *has not to be examined for*, the *washed precipitate* is at once examined according to Table VI and par. 294.

359. When the FIFH GROUP *has to be examined for*, the *washed precipitate* must be treated with boiling solution of NaHO; the members of the SIXTH GROUP are *insoluble*, but the members of the FIFTH are *soluble* in NaHO; if any of the precipitate is insoluble in it, filter, and treat the *insoluble portion* according to par. 360. *Examine the* NaHO *solution for the 5th group according to* par. 361.

360. The portion of the precipitate insoluble in NaHO must be examined, after it has been well washed, according to Table VI and par. 294.

361. To the NaHO solution must be added HCl in excess. If a precipitate is produced, on the addition of HCl, the colour of which is *white*, this arises merely from the separation of S, *none of the members of the group being present;* if the precipitate is of a *yellow* or *orange colour*, Sb_2S_3, SnS_2, and As_2S_3,* can only be present. If the colour of the precipitate is *black*, then all the members of the group must be sought for. The precipitate, after being well washed with hot water, must be examined according to the directions given under the 5th group (par. 213). *Before passing the* H_2S *through the solution consult* pars. 379, 380, and 381.

362. The *filtrate* from the H_2S precipitate, or the *solution* with which it has failed to give a precipitate, must be boiled until a piece of bibulous paper moistened with a solution of a lead salt *does not alter in colour* when held over it, a proof that all the H_2S is expelled. If boiling the liquid causes a separation of S, the solution, after the H_2S is expelled, must be

---

* For the colour of the sulphides of this group see par. 224.

filtered, and then examined for the *4th group* as directed in the next par.

363. THE FOURTH GROUP.—Before adding to the solution the *general reagent* for this group, a small portion of the solution must be tested for FeO, by adding to it a few drops of a solution of $K_6Fe_2Cy_{12}$,[*] observing the precautions mentioned in par. 177. When FeO is present the remainder of the solution must be boiled in an evaporating dish with a few drops of HNO_3, until all the FeO is converted into Fe_2O_3, which is accomplished when a drop of the solution does not give a blue colour with $K_6F_2Cy_{12}$. When FeO is not present, the solution does not require to be boiled with HNO_3, but it may at once be examined for the 4th group as directed in the next par.

364. NH_4Cl and NH_4HO must then be added to the solution; the NH_4HO must be added until the solution smells of it after it has been shaken. Warm the solution after the addition of the NH_4HO, and when a precipitate is produced collect it upon a filter, wash it with hot water until the wash-water does not turn red test-paper blue; examine it then according to Table IV and par. 156. *Before adding the* NH_4Cl *and* NH_4HO *consult* pars. 382, 383, and 384.

365. The *filtrate* from the precipitate produced by NH_4HO, or the *solution* with which it has failed to give a precipitate, must be examined for the THIRD GROUP according to the method described in the next par.

366. THIRD GROUP.[†]—$(NH_4)_2S$ [‡] must be added to the

---

[*] $K_6Fe_2Cy_{12}$ precipitates other oxides besides the FeO, but with no other oxide but FeO does it give a *blue* precipitate.

[†] Although FeO belongs, on account of its general properties, to this group, we have placed it in the special table of the 4th; because, in separating the groups, it is converted by HNO_3 into Fe_2O_3—a member of the 4th: we have thought it advisable, therefore, to contrast its special properties with the members of that group.

[‡] When the student does not look for the members of the three previous groups, viz. the 6th, 5th, and 4th, he must, before adding $(NH_4)_2S$ to the solution, add NH_4Cl and NH_4HO; in other words, he must add them to the solution which he has to examine for the members of the 3rd group, if they have not been added in the previous course of the analysis. The NH_4Cl is added, to prevent the precipitation of MgO by NH_4HO.

TABLE VII.—BEHAVIOUR OF THE BASIC GROUPS

FIRST GROUP. K_2O, Na_2O, $(NH_4)_2O$.	SECOND GROUP. *First Division.* BaO, SrO, CaO.	SECOND GROUP. *Second Division.* MgO.	THIRD GROUP MnO, ZnO, CoO, NiO, FeO.
1. HCl *does not* precipitate the members of this group from their solutions, because their *chlorides are soluble.*	1. HCl *does not* precipitate the members of this group from their solutions, because *their chlorides are soluble.*		1. HCl *does not* precipitate the members of this group from their solutions, because *their chlorides are soluble.*
2. H_2S *does not* precipitate the members of this group, either from their NEUTRAL, ACID, or ALKALINE solutions, because *their sulphides are soluble.*	2. H_2S *does not* precipitate the members of this group either from their NEUTRAL, ACID, or ALKALINE solutions, because *their sulphides are soluble.*		2. H_2S *does not* precipitate the members of this group from their ACID solutions
3. NH_4HO *does not* precipitate either of the other two members of the group.	3. NH_4HO *does not** precipitate the members of this division from their solutions.	3. NH_4HO *precipitates* Mg *partly* from its solutions as MgH_2O_2; the presence of AMMONIC SALTS *prevents** the precipitation.	3. NH_4HO *precipitates* the members of this group as HYDRATES In an excess of the reagent ZnH_2O_2, CoH_2O_2, and NiH_2O_2, are *readily soluble*, but MnH_2O_2 and FeH_2O_2 are insoluble but the presence of AMMONIC SALTS prevents *their precipitation.*
4. $(NH_4)_2S$ *does not* precipitate the other two members of this group from their solutions, because their *sulphides are* soluble.	4. $(NH_4)_2S$ *does not* precipitate the members of this group from their solutions, because *their sulphides are soluble.*		4. $(NH_4)_2S$ *precipitates* the members of this group from NEUTRAL and ALKALINE solutions, as *sulphides*
5. $(NH_4)_2CO_3$ *does not* precipitate either of the other two members of this group from their solutions.	5. $(NH_4)_2CO_3$ *precipitates* the members of this division from solutions as CARBONATES; the presence of AMMONIC SALTS *does not interfere* with their precipitation.	5. $(HH_4)_2CO_3$ *precipitates* Mg *only partly*, and the presence of AMMONIC SALTS *prevents* the precipitation.	5. $(NH_4)_2CO_3$ *precipitates* the members of the group; but they *are* with the exception of the Mn and Fe precipitates *readily soluble* in an *excess* of the reagent.
6. Na_2HPO_4 *does not* precipitate the other two members of this group from their solutions.	6. Na_2HPO_4 *precipitates* the members of this division from NEUTRAL and ALKALINE solutions, as PHOSPHATES.	6. Na_2HPO_4 *precipitates* Mg from its NEUTRAL and ALKALINE solutions, as PHOSPHATE; violent agitation promotes the formation of the precipitate. The precipitate is more soluble in *hot* than in *cold* water.	6. Na_2HPO_4 *precipitates* the members of this group from their NEUTRAL solutions as PHOSPHATES.

---

* The baric, strontic, and calcic phosphates and oxalates, and magnesic phosphate, are soluble in dilute mineral acids, but insoluble in water and the alkalies; consequently, when their acid solutions are rendered neutral or alkaline by ammonia, *these salts* are precipitated; therefore, when baryta, strontia, and lime are in combination with phosphoric and oxalic acids, and when magnesia is in combi-

FOURTH GROUP.	FIFTH GROUP.	SIXTH GROUP.	
		Second Division.	*First Division.*
Al_2O_3, Cr_2O_3, Fe_2O_3.	SnO, SnO_2, Sb_2O_3, As_2O_3, As_2O_5, Au_2O_3, PtO_2.	HgO, PbO, Bi_2O_3, CdO, CuO.	PbO, Ag_2O, Hg_2O.
1. HCl *does not* precipitate the members of this group from their solutions, because *their chlorides are soluble.*	1. HCl *does not* precipitate the members of this group from their solutions, because their *chlorides are soluble.*	1. HCl *does not* precipitate the members of this division of the group, because *their chlorides are soluble.*	1. HCl *precipitates* the members of this division, because *their chlorides are insolubte.* PbCl is slightly soluble in water; it is more soluble in hot than cold water.
2. H_2S *does not* precipitate any of the members of this group from their ACID solutions, for FeS is readily soluble in acids, and Al_2S_3 and Cr_2S_3 are not formed in the humid way.	2. H_2S *precipitates* all the members of this group from their ACID solutions, as *sulphides.*	2. H_2S *precipitates* all the members of this group from their NEUTRAL, ALKALINE, and ACID solutions, as *sulphides.*	
3. NH_4HO, *even in the presence of its salts,* precipitates the members of this group as HYDRATES,† which an *excess* of the reagent *does not* redissolve.	3. NH_4HO *precipitates* SOME of the members of this group.	3. NH_4HO *precipitates* the members of this group; but *in an excess* of the reagent the Ag, Cd, and Cu precipitates redissolve readily; but the Hg, Pb, and Bi precipitates are *insoluble* in an excess of the reagent.	
4. $(NH_4)_2S$ *precipitates* the members of this group from NEUTRAL and ALKALINE solutions; Fe''' as FeS, Al and Cr as $Al_2H_6O_6$ and $Cr_2H_6O_6$.	4. $(NH_4)_2S$, *if added in excess*, does not precipitate the members of this group from their solutions, because their SULPHIDES are soluble in the *alkaline sulphides.*	4. $(NH_4)_2S$ *precipitates* the members of this group from their NEUTRAL and ALKALINE solutions, as *sulphides.*	
5. $(NH_4)_2CO_3$ *precipitates* the members of this group from their solutions as OXIDES; an *excess* of the reagent *does not* redissolve them.	5. $(NH_4)_2CO_3$ *precipitates* SOME of the members of this group, as OXIDES.	5. $(NH_4)_2CO_3$ *precipitates* the members of this group from their solutions; and an excess of the reagent *does not* redissolve them, with the *exception* of the *cupric* precipitate.	
6. Na_2HPO_4 *precipitates* the members of this group from their NEUTRAL solutions as PHOSPHATES.	6. Na_2HPO_4 *precipitates* SOME of the members of this group from their NEUTRAL solutions as PHOSPHATES.	6. Na_2HPO_4 *precipitates* the members of this group from their NEUTRAL solutions, as PHOSPHATES.	

---

tion with phosphoric acid, they are precipitated in combination with these acids by ammonia, from their acid solutions, along with the members of the fourth group.

† When the iron, chromic, and aluminic phosphates are present in a solution, they are precipitated as phosphates, and not as hydrates, by ammonia.

solution, the liquid must afterwards be shaken and *gently* heated for some time. *When a precipitate is produced,* collect it upon a filter, and examine it according to Table III and par. 112. Before filtering the whole of the solution, add to that portion of the liquid which has been filtered, a little more $(NH_4)_2S$; if the reagent produces a further precipitate, add some to the unfiltered as well as to the filtered portion, refilter, and again test the filtrate with it. If the $(NH_4)_2S$ causes no precipitate in the filtered liquid, proceed with the filtration, as the group has been completely precipitated. *Before adding* $(NH_4)_2S$ *to the solution consult* pars. 385, 386, 387.

367. If the *filtrate* from the $(NH_4)_2S$ precipitate, or the *solution* with which it has failed to give a precipitate, has become, from its addition, of a *dark brown* colour, the filtrate or solution must be evaporated and then acidified with HCl, and filtered as directed in par. 387. NH_4HO in excess must be added to the filtrate, which must then be examined for the SECOND GROUP according to par. 369.

368. If the *filtrate* from the $(NH_4)_2S$ precipitate, or the *solution* with which it has failed to give a precipitate, has not *altered in colour,* it can at once be examined for the SECOND GROUP as directed in the next par.

369. FIRST DIVISION OF THE SECOND GROUP.—$(NH_4)_2CO_3$* must be added to the solution; the solution must then be gently warmed for some time, *but not boiled.* If one or all

---

* When the student does not look for the members of the four previous groups, viz. the 6th, 5th, 4th, and 3rd, he must, before adding the $(NH_4)_2CO_3$ to the solution, add NH_4Cl and NH_4HO; in other words, he must add them to the solution which he has to examine for the members of the second group, if they have not been added in the previous course of the analysis. The NH_4Cl is added to prevent the precipitation of the MgO by the carbonate of ammonia; any ammonic salt may be employed, the acid of which forms no insoluble compound with MgO or the other members of the group. If the ammonic carbonate employed is an acid carbonate, a portion of the alkaline earths is apt to be dissolved by it. The NH_4HO is added to prevent this; it does so by converting it into a neutral carbonate.

of the members of this division are present, a precipitate will be produced by the $(NH_4)_2CO_3$, especially after warming the solution. *When a precipitate is produced*, collect it upon a filter and wash it with hot water, and afterwards examine it according to Table II and par. 66. Before filtering the whole of the solution, add to that portion of the liquid which has been filtered a little more $(NH_4)_2CO_3$; if the reagent produces a further precipitate, add some to the unfiltered as well as to the filtered portion, re-filter, and again test the filtrate with it. If the $(NH_4)_2CO_3$ causes no precipitate in the filtered liquid, proceed with the filtration, as the group has been completely precipitated. *Before adding the* $(NH_4)_2CO_3$, *consult* pars. 388 and 389.

370. The *filtrate* from the precipitate produced by $(NH_4)_2CO_3$, or the *solution* with which it has failed to give a precipitate, must be examined for Mg, K, and Na, as directed in the next par.

371. The solution which has to be examined for Mg, K and Na must be divided into two parts, which we shall call A and B.

372. The A portion may be employed for the examination for Mg; for this purpose we must add to the solution, which must be quite cold, Na_2HPO_4 and also NH_4HO, if this latter reagent is not already present in the solution, the liquid after the addition of the reagent ought to be shaken very violently; and if, after time (one or two hours) has been allowed for the formation of the precipitate, *there is no precipitate*, Mg *is absent.* If *there is a precipitate*, Mg *is present. Before adding* Na_2HPO_4, *consult* pars. 390 and 391.

373. Examine B for K and Na according to par 27.

374. When a precipitate has been produced by $(NH_4)_2CO_3$, one drop of dilute H_2SO_4 ought to be added to the B solution before it is evaporated and ignited. The acid is added to remove the minute quantity of Sr, if present, which remains unprecipitated by $(NH_4)_2CO_3$, as Sr imparts to the flame a colour very similar to that produced by K.

375. AMMONIA. A portion of the *original* solution must be examined for ammonia according to par. 24.

PARTICULAR OBSERVATIONS REGARDING THE PRECIPITATES PRODUCED BY THE GROUP REAGENTS, AND THE PRECAUTIONS TO BE OBSERVED IN EXAMINING FOR THE DIFFERENT GROUPS.

376. *Precautions to be attended to in examining for the first section of the Sixth Group.*—Before adding HCl to the solution under examination, it is necessary to ascertain, by test-papers, whether the solution is acid, neutral, or alkaline. When it is one of the two former, a few drops of the acid will generally be sufficient; if alkaline, the acid must be added until it is decidedly in excess. When a precipitate is produced, add the acid, drop by drop, until it ceases to increase; then add a few drops more, shake the mixture, and filter. When no precipitate is produced, a few drops of the acid will in most cases be sufficient, since our only object in adding it then is to acidify the solution, in order to prevent the precipitation of the 3rd and 4th groups by H_2S. *When evolution of gas takes place on the addition of* HCl, examine it for CO_2, H_2S, and HCy, as directed under those heads.

377. As Ag is not precipitated, under certain circumstances, by HCl—and as a precipitate may be produced on the addition of HCl, in the absence of Ag_2O, PbO, and Hg_2O—it is requisite to notice, 1st, the substances which interfere with the precipitation of Ag; 2nd, the substances which may be precipitated, and under what condition the precipitation takes place. 1st. When $Hg(NO_3)_2$ is present in the solution, Ag, if present, will not be precipitated by HCl, because AgCl is soluble in a solution of $Hg(NO_3)_2$, especially if the solution is hot and concentrated; on the addition of water and cooling, the solution may deposit shining yellowish-white crystals, which are pure AgCl. When $Hg(NO_3)_2$ is suspected to be present, ammonic acetate ought to be added to the solution

after the addition of the HCl, as this ensures the complete precipitation of the AgCl. 2nd. The precipitate* may be occasioned by the presence of some salt of Sb or Bi, as $SbCl_3$ and $BiCl_3$ are decomposed by much water into soluble acid and insoluble basic salts. The precipitate† may also arise from the presence of some substance insoluble in water, but soluble in the caustic, carbonated, or sulphuretted alkalies, or in an alkaline cyanide—for example, phosphate of alumina, or alumina dissolved in NaHO, As_2S_3 dissolved in NH_4HCO_3, Sb_2S_3 dissolved in an alkaline sulphide, $NiCy_2$ dissolved in an alkaline cyanide, AgCl dissolved in NH_4HO; or the precipitate may be due to silicic acid, some alkaline silicate being present. If the precipitate is due either to Sb or Bi, it will redissolve on the addition of a few drops more of HCl. When silicic acid is the substance thrown down, the precipitate will appear very gelatinous, and will remain undissolved on the further addition of acid; a fresh portion of the original solution must, therefore, be acidulated with HNO_3, and evaporated to dryness to render the silicic acid insoluble; the ignited mass may then be digested with dilute HNO_3, and filtered.‡ The analysis of the filtrate must then be conducted in the regular way, by adding to it HCl, &c. If the precipitate should be due to the presence of any of the other substances, a fresh portion of the original solution ought to be taken, and HNO_3 added to it until it is decidedly acid. If the precipitate does not disappear on the addition of the acid, the solution ought to be warmed; if this should fail to dissolve the precipitate, it must be collected upon a filter, and examined as a substance insoluble in water and acids (*see* 719).

---

* If the HCl employed contain a trace of H_2SO_4 and Ba be present in the fluid under examination, a slight trace of insoluble $BaSO_4$ will be formed, which may be distinguished by the difficulty experienced in separating it from the fluid by filtration.

† HCl precipitates, of the inorganic acids, boracic acid; and of the organic acids, benzoic and uric acids, if the solution is very concentrated. The two former are dissolved by hot water, and the uric acid by heating with HNO_3.

‡ The precipitate left upon the filter must be examined for silicic acid according to the method described under the head of that acid.

378. As the $PbCl_2$, $AgCl$, and $HgCl$ are very heavy, they easily separate from the solution; there is, therefore, no need to warm the fluid to effect this object. Indeed, it would be disadvantageous to do so, as a portion of the $HgCl$ would be converted into $HgCl_2$, and the greater portion, if not all, the $PbCl_2$ would be dissolved.

379. *Precautions to be observed in examining for the second section of the Sixth and the whole of the Fifth Group.*—Before passing H_2S through the solution it will be necessary to dilute it with water, if it be very acid, as the members of the two groups are not readily precipitated as sulphides from very acid solutions. Especially is it very difficult to precipitate Cd by H_2S in the presence of much HCl. If, therefore, the solution has not been diluted, and Cd is present, a yellow precipitate may be obtained on adding $(NH_4)_2S$ to precipitate the 3rd group. It must also be observed that if the solution has not been rendered sufficiently acid, some of the Zn, if it be present, may be precipitated by H_2S. If on diluting the liquid it becomes turbid, this arises from the presence of some salt of Sb or Bi; a few drops of acid will redissolve this precipitate. Arsenic acid is reduced very slowly by H_2S, but SO_2* reduces it rapidly, if assisted by a gentle heat; if, therefore, arsenic acid is present or its presence suspected, SO_2 ought to be added in excess, the solution then gently warmed for some time, and finally boiled until the excess of SO_2 is expelled. If Zn is present, and the arsenic acid has not been reduced, a precipitate would be produced having this composition, $ZnAs_2S_6$.

380. If, on the addition of H_2S, no precipitate be produced, it proves the absence of the 2nd section of the 6th and the whole of the 5th group. If a precipitate be produced, the colour of

---

* If Ba, Sr, or Pb, be present, the SO_2 will give rise to a precipitation of their sulphates; the precipitate should be collected upon a filter, washed, dried, and then examined as a substance insoluble in water and acids, according to 729.

which is white,* this likewise proves the absence of these groups, as the white precipitate is merely due to a separation of S, occasioned by some of the H_2S being decomposed by its reducing some higher oxide to a lower degree of oxidation. If the colour of the solution, originally *orange* or *yellow*, change to a *green*, after the gas is passed through it, the separation of sulphur is due to the reduction of CrO_3 to Cr_2O_3; the white S suspended in the green solution frequently perplexes the student, as it appears at first like a green precipitate. If the separation of S be not attended with any change in colour, it is (probably) attributable to the reduction of Fe_2O_3 to FeO, CrO_3 and Fe_2O_3 being both found in their lower degree of oxidation after H_2S or any reducing agent has been added to their solutions.

381. If on the first transmission of H_2S through the solution a *white* precipitate be formed, which, on a further addition of the reagent, acquires *an orange colour*, and becomes finally *black*, it points out that some mercuric salt is present. If the precipitate, on its first formation, assumes a red or brownish-red colour, and becomes finally black, it indicates the probable presence of some lead salt.

382. *Precautions to be observed in examining for the Fourth Group.*—If the H_2S were not expelled before boiling the solution with HNO_3, the latter would give rise, by oxidation of the S, to H_2SO_4, which would precipitate Ba and Sr, and possibly Ca, as sulphates, if they were present. Even when HNO_3 has not to be added to the solution, no FeO being present, it is necessary to expel the H_2S before adding NH_4HO, otherwise $(NH_4)_2S$ would be formed, and consequently the third as well as the fourth group would be precipitated. When the solution is very acid, no NH_4Cl need be added, as a

---

* If HNO_3 be present in the solution, a thick tenacious yellow mass of sulphur will separate, occasioned by the decomposition of the H_2S by the acid. When such is the case, the gas has to be passed through the solution for some time before its characteristic odour will be imparted to the liquid, showing that a sufficient quantity has been added. $HClO_3$ and free Cl decompose H_2S in the same way as HNO_3.

sufficient amount of ammonic salt will be formed on the addition of the NH_4HO.

383. When much Cr_2O_3 is present, a small quantity will frequently dissolve in the NH_4HO, and will impart to the fluid a puce-red tint. When this occurs, it is difficult to remove the last traces of Cr from the solution. If warming the solution fail, it is better to disregard it; for if the solution were evaporated to effect the object, a greater or less quantity of the oxides of Mn, Ni, and Co, if they were present, would be precipitated.

384. The precipitate produced by NH_4HO may consist, in addition to the members of the fourth group, of the following salts:—Al, Cr''', Fe, Mn, Ba, Sr, Ca, and Mg, in combination with PO_4; and Ba, Sr, and Ca, in combination with C_2O_4. When the student looks for acids as well as bases, he must examine the precipitate produced by NH_4HO, according to Table V, or pars. 191, 197, or 198. Ba, Sr, and Ca, in combination with F and BO_3, may also be precipitated by NH_4HO in minute quantities; but as a sufficient quantity of the bases will always remain in solution, and be precipitated as members of the 2nd group, and as the acids will be found in the examination for acids, we have not included these salts in the table.

385. *Precautions to be observed in examining for the Third Group.*—If CrO_3 and Ba are both present in solution, a substance insoluble in acids is sometimes formed on dissolving the precipitate produced by NH_4HO, or that produced by $(NH_4)_2S$; the insoluble substance is $BaSO_4$. A sulphur acid appears to be formed when CrO_3 is reduced by H_2S, which becomes converted into SO_4 after some time.

386. The precipitate produced by $(NH_4)_2S$ is very difficult to filter; the filtrate will frequently come through the filter *turbid* for some time; there is no remedy for this but to pass it through the filter until it is perfectly clear. The student must not mistake between a *turbid filtrate* and one which is *perfectly clear but coloured.* A filter can only remove what is held in suspension by a liquid, as in the first case; it cannot remove

what is dissolved, as in the second case; when the filtrate is coloured, consult the next par. The precipitate must be carefully washed with water containing a little $(NH_4)_2S$, in order to prevent the precipitated sulphides from oxidizing. If the wash-water comes through of a deep-brown colour, it must be treated as directed in the next par.

387. If the filtrate from the $(NH_4)_2S$ precipitate be of a very dark-brown colour, it is occasioned by the presence of Ni, the sulphide of that metal being slightly soluble in $(NH_4)_2S$. When a considerable portion of this substance has passed into solution, the filtrate, and likewise the wash-water if it is dark coloured, must be evaporated until the excess of $(NH_4)_2S$ is expelled; the solution is then acidified with dilute HCl, and the black precipitate which separates on the addition of the acid collected upon a filter, and examined with that previously obtained. If Cd has not been completely precipitated by H_2S, the precipitate by $(NH_4)_2S$ may be yellow in colour from the presence of CdS.

388. *Precautions to be observed in examining for the first division of the Second Group.*—After the addition of the $(NH_4)_2CO_3$, the solution should be heated gently, but not boiled, since the NH_4Cl might then decompose and dissolve some of the precipitated carbonates.

389. Although $(NH_4)_2CO_3$ does not precipitate completely Ba, Sr, and Ca from their solutions, especially when the quantity of ammonic salts present is considerable, it is sufficiently exact for all ordinary qualitative purposes. "The separation is never perfect, owing to the solvent action which ammonic salts exercise, more especially upon $BaCO_3$ and $CaCO_3$; indeed, minute traces of Ba and Ca can rarely be precipitated in this manner. Ba is separated the most completely by H_2SO_4 or a sulphate; Ca by $(NH_4)_2C_2O_4$, in presence of NH_4HO and some NH_4Cl; Sr same manner as Ca, or by NH_4HO and $(NH_4)_2CO_3$ in presence of NH_4Cl."

390. *Precautions to be observed in examining for the second division of the Second Group.*—If the solution has become very dilute during the course of the analysis, it will render the

detection of the Mg more certain, if, before adding the Na_2HPO_4, the solution is concentrated. In any case, time must be allowed for the formation of the precipitate, the solution must be quite cold when the reagent is added, and after the addition of the reagent the solution must be frequently shaken; as $MgNH_4PO_4$ is more insoluble in water containing NH_4HO than in pure water, it is necessary to have NH_4HO in excess.

391. Frequently a flocculent precipitate is obtained on the addition of Na_2HPO_4, which is not due to the presence of Mg; Bloxam states that it is aluminic phosphate, but I have found that it is sometimes due to calcic phosphate arising from the lime in the filter-paper.

392. Answers to the following exercises must be written out.

EXERCISES.

135. What are the characters of the solutions of salts of Mn, Cu, Pb, Fe'', and Fe''' ?

136. What are the characteristic reactions by which you would distinguish, by the blowpipe, ores of lead, bismuth, zinc, and antimony ?

137. Express by means of equations the action of HNO_3 of different strengths on Zn, Fe, Cu, Ag, Sn, and Hg respectively; also the action of H_2SO_4 and HCl on these metals.

138. Separate, 1st, into groups, and, 2ndly, from each other, the following substances:—Cu, Mn, Ba, Al, Cd, NH_4, Zn, K, and Ca; confirm the presence of each by means of a characteristic reagent.

139. Classify the following metals into those which (*a*) decompose water in the cold, (*b*) at the boiling temperature, (*c*) at a red heat, and (*d*) not at all:

Pt, K, Zn, Mg, Cu, Mn, Al, Ag, Fe.

140. A solution acid to test-paper gives an orange precipitate by the action of H_2S: what substances must be absent, what may the precipitate contain, and how would you examine it ?

141. Classify the following oxides into those which (*a*) are reduced to the metallic state by heat alone, (*b*) are not reduced by heat alone, (*c*) are not reduced by charcoal alone, (*d*) are reduced by charcoal, (*e*) are reduced by H, (*f*) are not reduced by H, (*g*) are reduced by CO:

Bi_2O_3, PbO_2, Fe_2O_3, K_2O, Al_2O_3, As_2O_5, MnO, MgO,
Au_2O_3, FeO, SnO_2, BaO, CoO.

142. Do the sulphides of the 5th group experience any change when dissolved in a solution of KHO or NaHO?

ACIDS.

393. The acids may be divided into two classes, the INORGANIC and the ORGANIC. All the organic acids contain carbon as a constituent, and they and their salts are decomposed by heat, the metals of the salts being left, when they are the alkaline or alkaline earth metals, in the state of carbonates; the decomposition of the organic acids or their salts by heat is also attended in the majority of cases with the separation of carbon.

394. Acids, both organic and inorganic, do not admit of that accurate classification into groups which is the case with bases, many of them being members of more than one group.

INORGANIC ACIDS.*

395. The special properties of each acid are first described; then their division into groups, with a description of the properties of each group of acids; and finally the processes to be followed in preparing the solutions for the examination of the inorganic acids, and the methods to be pursued in the examination.

396. The student must make the experiments given under the head of each acid, and then test the behaviour of the acids with the group reagents; after he has made these experiments

---

* Oxalic acid, although an organic acid, has, on account of its frequent occurrence, been treated along with the inorganic acids.

he passes over the organic acids and proceeds to the *examination of liquids.*

BEHAVIOUR OF THE ACIDS AND THEIR RADICALS WITH REAGENTS.

CHROMIC ACID, H_2CrO_4.

Solution for the reactions, K_2CrO_4 *in water.*

397. This acid has not been obtained in the solid state; it is supposed to exist in solution. CHROMIC ANHYDRIDE (CrO_3) is a crystalline scarlet-coloured solid, which deliquesces rapidly when exposed to the air; its solution possesses a deep reddish-brown tint. CrO_3 may be obtained by adding undiluted H_2SO_4 to a concentrated solution of $K_2Cr_2O_7$. CrO_3 melts at 190° C.; at higher temperatures it is decomposed into Cr_2O_3 and O.

398. There are *normal, acid* and *basic chromates.* The normal salts of the alkalies, of Ca, Sr, Mg, Ni, Zn, and Cu, are soluble in water; the normal salts of the other metals are insoluble in H_2O, but they are nearly all soluble in HNO_3; all the acid chromates are soluble in water. There are two acid chromates of potash, viz. the bichromate K_2CrO_4, CrO_3 or $K_2Cr_2O_7$, and the terchromate $K_2CrO_4, 2CrO_3$ or $K_2Cr_3O_{10}$. The normal chromates of the alkalies and alkaline earths are *yellow,* the bichromates are *red.* The chromates of the heavy metals are *bright yellow, red,* or *brown;* the aqueous solutions of the soluble salts are the same colour as the salts themselves; the *yellow* of the solution of a normal chromate changes, on the addition of an acid, to *red,* owing to the formation of an acid chromate. The solution of the normal chromates of the alkalies are *alkaline,* and the bichromates are *acid,* to test-paper. Alkaline chromates may be prepared from insoluble chromates by fusing the latter in conjunction with alkaline carbonates or nitrates.

399. The normal alkaline chromates are not decomposed even at a full red heat. The normal chromates of the weaker bases are decomposed by heat, the CrO_3 being decomposed

into Cr_2O_3 and O; the acid chromates of the alkalies are decomposed by heat, a mixture of normal chromate and Cr_2O_3 being left, and O given off. All the chromates are decomposed on being heated with undiluted H_2SO_4; chromic sulphate and another sulphate being formed and O given off, thus:

$$2K_2CrO_4 + 5H_2SO_4 = Cr_23SO_4 + 2K_2SO_4 + 5H_2O + O_3$$

They are also decomposed on being heated with HCl, chromic chloride and another chloride being formed and Cl evolved, thus:

$$2K_2CrO_4 + 16HCl = Cr_2Cl_6 + 4KCl + 8H_2O + 3Cl_2$$

CrO_3 and the chromates are also decomposed by H_2S, Cr_2O_3 and H_2O being formed and S set free; they are reduced by SO_2, and also on being heated with $H_2\overline{T}$, $H_2\overline{O}$, and by many other substances; on account of the facility with which CrO_3 is reduced to Cr_2O_3, it possesses considerable oxidizing power. All these reactions are characterised by the change of colour of the solution from a *red* or *yellow* to *green*. As H_2S converts CrO_3 into Cr_2O_3, we always obtain the CrO_3 in the form of Cr_2O_3 in testing for the bases.

400. If a very dilute acid solution of hydric peroxide (H_2O_2)* is covered with a layer of ether, and a fluid containing chromic acid is added, the solution of H_2O_2 acquires a fine blue colour. By inverting the test-tube closed with the thumb, repeatedly, without much shaking, the solution becomes colourless, whilst the ether acquires a blue colour. The latter reaction is particularly characteristic. One part of potassic chromate in 40,000 parts of water suffices to produce it distinctly; the presence of vanadic acid materially impairs the delicacy of the

---

* Solution of H_2O_2 may be easily prepared by triturating a fragment of baric peroxide (BaO_2), about the size of a pea, with some water, and then adding a little dilute HCl. The solution keeps a long time without suffering decomposition. In default of BaO_2, impure Na_2O_2 may be used instead, which is obtained by heating a fragment of Na in a small porcelain dish until it takes fire, and letting it burn.

test. After some time reduction of the CrO_3 to Cr_2O_3 takes place, and at the same time decoloration of the ether.—***Fresenius.***

SULPHURIC ACID, H_2SO_4.

Solution for the reactions, Na_2SO_4 *in water.*

401. H_2SO_4 is a heavy colourless fluid, of an oily appearance, which possesses a strong affinity for H_2O, producing when mixed with it a great degree of heat. Its affinity for H_2O is so great, that it decomposes organic substances when placed in contact with them, removing their H and O, whilst the C is left behind as a black coaly mass, a portion of which dissolves in the acid and communicates to it a brown tint. If heat is applied, the C is oxidized at the expense of the acid, CO_2 and SO_2 being formed; these facts may be illustrated by pouring some strong acid upon white sugar. H_2SO_4, at temperatures below its boiling-point (327° C.), displaces all other acids from their combinations with bases, but above that temperature it is itself displaced by the non-volatile acids. SULPHURIC ANHYDRIDE (SO_3) is a white solid, similar in appearance to asbestos. It evaporates and emits dense fumes on exposure to air. Its affinity for H_2O is so great, that it hisses like red-hot iron when brought in contact with it.

402. As H_2SO_4 is bibasic, it forms with monatomic metals two classes of salts, viz. *neutral* salts, M_2SO_4, and *acid* salts, $MHSO_4$. The solutions of the neutral sulphates of the alkalies, of Ca, Mg, Mn, and Ag are *neutral* to test-paper; the neutral sulphates of the other bases and the acid sulphates of the alkalies are *acid* to test-paper. $BaSO_4$, $PbSO_4$ are *insoluble*, $SrSO_4$, $CaSO_4$ are *nearly insoluble*, all the other sulphates are *soluble*, in water. Neither $PbSO_4$ nor the sulphates of the metals of the alkalies and alkaline earths are decomposed when heated to redness, except $MgSO_4$, which loses its acid partially. The sulphates of Zn, Cd, Ni, Co, Cu, and Ag require an intense heat to decompose them; but the other sulphates part with their acid without difficulty when strongly ignited. All the sulphates, on being mixed with charcoal and heated,

are decomposed; the sulphates of the metals of the alkalies and alkaline earths, and lead are reduced to sulphides. The other sulphates evolve SO_2, which may be detected by the smell, and by its bleaching moist Brazil-wood paper.

403. Sulphates in dilute solutions containing organic matter are gradually converted into sulphides. Water containing a sulphate may therefore, after it has been kept a long time in a bottle or any closed vessel, be found to contain H_2S, although originally it was perfectly free from it.

404. $BaSO_4$ is distinguished from all other baric salts, but baric selenate and baric fluosilicate, by *its insolubility in dilute acids*. Any *soluble baric salt* is therefore the best and most delicate test for H_2SO_4, whether free or combined, the solution being acidified with dilute HCl or dilute HNO_3 before adding the baric salt.

405. Insoluble sulphates are completely decomposed by fusion with *alkaline carbonates*, an ALKALINE SULPHATE being produced along with a CARBONATE or an OXIDE of the other METAL.

406. When a sulphate, mixed with C and Na_2CO_3, is fused upon a charcoal support by the inner blowpipe flame, Na_2S is produced. If the fused mass, moistened with water, be placed upon a piece of silver, a brown stain of Ag_2S will be formed.

407. "To detect free H_2SO_4 in presence of a sulphate, the fluid under examination is mixed with a very little cane-sugar, and the mixture evaporated to dryness in a porcelain dish at 100° C. If free H_2SO_4 was present a black residue remains, or, in the case of most minute quantities, a blackish-green residue. Other acids do not decompose cane-sugar in this way."

SULPHUROUS ACID, H_2SO_3.

408. This acid is formed when SO_2 is passed into water; it attracts oxygen from the air, and becomes converted into H_2SO_4. Sulphurous anhydride (SO_2) is a colourless gas. The acid and the anhydride have the odour of burning sulphur; they act as powerful reducing agents; they

redden litmus paper and blanch Brazil-wood paper. The sulphites are decomposed by nearly all acids, save carbonic and boracic acids, with the liberation of sulphurous acid.

409. $BaCl_2$ and $CaCl_2$ produce white precipitates in solutions of the sulphites soluble in HCl.

410. $AgNO_3$ produces a white precipitate in solutions of sulphites of Ag_2SO_3, which decomposes on the application of heat, becoming black: $Ag_2SO_3 + H_2O = H_2SO_4 + Ag_2$.

411. The smallest trace of SO_2 in a gaseous mixture or of free H_2SO_3 may be detected by means of strips of paper steeped in starch-paste, to which a small quantity of iodic acid or potassic iodate has been added. The iodic acid is reduced, and the iodine set free, which forms with the starch the well-known blue compound.

412. Sulphites, when mixed with HCl and $SnCl_2$, produce a yellowish precipitate, SnS_2; sulphites treated with Zn and HCl evolve H_2S.

413. H_2S produces in solutions of H_2SO_3 a white precipitate of S, whilst in solution there remains pentathionic acid ($H_2S_5O_6$).

HYPOSULPHUROUS OR THIOSULPHURIC ACID, $H_2S_2O_3$.

414. This acid is scarcely known in its free state; it is generally considered to be almost immediately resolved into H_2SO_3 and S; but, according to Rose, it is comparatively stable in dilute solutions.

415. Solutions of hyposulphites give with *mercuric*, *plumbic*, and *argentic* salts white precipitates, which speedily become *yellow*, *brown*, and *black*.

416. Hyposulphites treated with HCl give off SO_2 and S, which in this case is yellow, not white. When the hyposulphites are treated with iodine an iodide and a tetrathionate are formed: $2BaS_2O_3 + I_2 = BaI_2 + BaS_4O_6$. These two reactions distinguish $H_2S_2O_3$ from H_2SO_3.

BORACIC ACID OR ORTHOBORACIC ACID, H_3BO_3.

Solution of borax, $2NaBO_2, B_2O_3$, *in water*.

417. This acid is best obtained on the small scale by adding to a boiling concentrated solution of borax concentrated H_2SO_4 or HCl until the liquid strongly reddens litmus; on cooling, the greater part of the acid separates from the solution in pearly looking scales, and on evaporating the mother-liquor another crop is obtained. The crystals retain a portion of the HCl or H_2SO_4; from the former they are freed by gentle heating and recrystallization, but to free them from the latter acid

they must be fused in a platinum crucible, and the fused mass crystallized. H_3BO_3 is sparingly soluble in cold water, but is dissolved by three times its weight of boiling water; its aqueous solution turns blue litmus-paper, not bright red, like other acids, but of a claret colour, and if the solution is allowed to evaporate on turmeric paper it turns the paper brown like the alkalies. It is soluble in alcohol, and the solution burns with a beautiful green-edged flame; this green colour is not produced if the acid is in combination with a base. On evaporating an alcoholic or aqueous solution of the acid a portion of it volatilizes with the vapour of the liquid, although it is not itself volatilized by heat. It decomposes solutions of the carbonates in the cold, but a brisk current of CO_2 or H_2S passed through a concentrated solution will cause a separation of boracic acid in crystals. At a temperature of 100° C. it is converted into meta- or monobasic boracic acid, HBO_2, thus—

$$H_3BO_3 = HBO_2 + H_2O$$

At a red heat it is converted into *boracic anhydrate*, B_2O_3, which is a brittle glassy solid; it volatilizes very slowly, even on intense ignition; at high temperatures it expels from salts all anhydrides more volatile than itself. It dissolves readily in water forming H_3BO_3.

418. H_3BO_3 is met with in its free state in many volcanic districts, especially in Tuscany, where it issues from the earth with the vapour of water. It is obtained in the form of crude borax, or tincal, from the salt lakes of India, Thibet, &c. "The borates are chiefly of two classes, namely, orthoborates (such as the normal trisodic borate, Na_3BO_3, and the penta-hydropotassic diborate, KH_52BO_3, and metaborates (such as the potassic metaborate, KBO_2)." The borates are not decomposed on ignition, they are colourless, and they all, even the salts that contain an excess of acid, manifest alkaline reaction with test-paper. They are all, with the exception of the alkali salts, almost totally insoluble in water, but they dissolve readily in acids and in water containing ammonic salts.

419. To detect a borate, add to the powdered substance

under examination *strong* H_2SO_4 and *alcohol* or *wood naphtha*; ignite the mixture subsequently. If a borate be present the borders of the flame will appear *green*, which becomes more distinct upon stirring, and the delicacy is further increased by repeatedly extinguishing and rekindling the flame. Copper salts impart the same colour to the flame; Cu, if present, ought to be precipitated by H_2S, before testing for H_3BO_3. Chlorides interfere also with the test.

420. If a solution of an alkaline borate is mixed with HCl to slight but distinct acid reaction, and a slip of *turmeric* paper is half dipped into it, and then dried at 100 C., the dipped half shows a peculiar red tint; this reaction is very delicate. Care must be taken not to confound this coloration with the blackish-brown which turmeric paper acquires when moistened with strong HCl and dried, nor with the brownish-red which Fe_2Cl_6 imparts to turmeric paper. By moistening turmeric paper reddened by H_3BO_3 with a solution of an alkali, the colour is changed to bluish-black or greenish-black; the addition of a little HCl restores the brownish-red colour.—*Fresenius.*

421. To detect the boracic oxide, reduce the substance to be examined for it to a very fine powder, and then mix thoroughly with it five parts of $KHSO_4$ and one part CaF_2, and fuse the mass by the blowpipe flame in the loop of the platinum wire; boric fluoride, BF_3 escapes and tinges the flame green for a few seconds.

PHOSPHORIC ACID OR ORTHOPHOSPHORIC ACID, H_3PO_4.

Solution of common sodic phosphate, Na_2HPO_4, *in water.*

422. H_3PO_4 may be obtained in the form of colourless crystals; they deliquesce rapidly in the air. The aqueous solution of H_3PO_4 has a strong acid reaction, and at a boiling heat expels most volatile acids from their combinations with bases. The aqueous solution may be heated to 160° C. without altering the character of the acid, but at 215° it is converted into the pyro-phosphoric acid, $H_4P_2O_7$, while above this temperature metaphosphoric acid, HPO_3, begins to be formed, and,

after the application of a full red heat, constitutes the entire residue. PHOSPHORIC ANHYDRIDE, P_2O_5, is obtained by burning P in dry O or dry air; it appears under the form of white flakes, which rapidly absorb moisture from the air. It is a powerful dehydrating agent. It forms, by contact with water, HPO_3, but if boiled with the water H_3PO_4. After the P_2O_5 has once been dissolved it cannot be converted back into the anhydride by heat.

423. The following are the general formulæ for the phosphates:—$M'H_2PO_4$; this class is frequently designated acid phosphates. M'_2HPO_4. $M''HPO_4$; these are frequently termed neutral phosphates. M_3PO_4, $M''MPO_4$, $M'''PO_4$, $M''_3(PO_4)_2$, these are termed tribasic phosphates, there are in addition basic phosphates. Na_3PO_4 and K_3PO_4 are soluble in water, their solutions are alkaline, and they are decomposed by CO_2, thus:— $Na_3PO_4 + CO_2 + H_2O = Na_2HPO_4 + NaHCO_3$. Na_2HPO_4 and K_2HPO_4 are soluble in water; their solutions have a feebly alkaline reaction. NaH_2PO_4, KH_2PO_4 are soluble in water; their solutions are strongly acid. The phosphates, with the exception of the alkaline ones, are nearly all insoluble in water.

424. $MgSO_4$, or *any soluble magnesic salt*, produces in aqueous solutions of the phosphates, if concentrated, a white precipitate of $MgHPO_4$. A salt much more insoluble in water is produced by adding NH_4Cl, NH_4HO, and then $MgSO_4$; the precipitate produced in this case is $MgNH_4PO_4$, which is slightly soluble in pure water, but almost insoluble in water containing NH_4HO. In dilute solutions it only appears *after much agitation and the lapse of some time*; agitation promotes its formation in all cases. This test can only be applied when the *phosphates* are soluble in *ammonic* solutions.

425. Plumbic acetate produces a white precipitate of $Pb_3(PO_4)_2$ soluble in HNO_3. If this precipitate, after being dried, is heated in the outer flame of the blowpipe, it becomes distinctly crystalline on cooling. This test is very characteristic, not only on account of the crystalline structure of the

bead, but also from the circumstance that the $Pb_3(PO_4)_2$ is the only lead salt which is not reduced to the metallic state when heated in the inner blowpipe flame. It is evident that, to render this test of any value, the $Pb_3(PO_4)_2$ must be freed thoroughly, by washing, from all lead acetate.

426. $AgNO_3$ throws down from solutions of phosphates containing one, two, or three atoms of fixed base, a light *yellow* precipitate of Ag_3PO_4, readily soluble in HNO_3 and in NH_4HO. If the solution contained a phosphate containing three atoms of fixed base, after the precipitation the solution will be *neutral* to test-paper, but *acid* if the phosphate contains one or two atoms of fixed base, on account of the HNO_3 that will be set free.

427. If to an acid solution of a phosphate containing the least possible excess of HCl or HNO_3 a tolerably large amount of sodic acetate is added, and then a drop of Fe_2Cl_6, a *yellowish-white* gelatinous precipitate of $Fe'''PO_4$ will be formed. An excess of Fe_2Cl_6 must be avoided, as ferric acetate would thereby be formed, in which $Fe'''PO_4$ is not insoluble. By this reaction the acid can be detected when combined with the alkaline earths, but it can only be held to be decisive in the absence of H_3AsO_4, as this acid forms a similar precipitate. To effect the complete separation of the acid from the alkaline earths, Fe_2Cl_6 is added until the solution begins to be of a reddish colour; it is then boiled, when the whole of the Fe is precipitated, partly as phosphate, partly as basic acetate. It must be filtered whilst hot; the filtrate contains the alkaline earths as chlorides. To detect by means of this reaction the acid in the presence of much Fe_2O_3, the HCl solution must be boiled with $NaHSO_3$ until the Fe_2Cl_6 is reduced to $FeCl_2$, which is indicated by the decoloration of the solution; add then Na_2CO_3 until the fluid is nearly neutral, afterwards sodic acetate, and finally one drop of Fe_2Cl_6. The reason for this proceeding is that $Fe''2\bar{A}$ does not dissolve $Fe'''PO_4$.

428. The solution of ammonic molybdate in HNO_3 produces, immediately, in neutral or acid solutions of phosphates in the cold, a finely divided *yellow* precipitate, unless the quantity of

phosphate is very minute; in that case the precipitate appears only after some hours, and the solution ought to be gently warmed. The precipitate is soluble in H_3PO_4 and other acids, but it is rendered insoluble in them by an excess of the reagent; an excess of the fluid containing the phosphates must, therefore, be avoided. By this method PO_4 can be separated from the metals of the alkaline earths, from Fe, Al, and other metals whose phosphates are insoluble in water. Presence of $H_2\overline{T}$ and other organic substances, and of large quantities of HCl, interferes with the precipitation. The precipitate is soluble in NH_4HO, and may, after it has been washed with the molybdic solution, be dissolved in it, and the PO_4 precipitated from the solution by adding NH_4Cl and $MgSO_4$. H_3AsO_4 gives no precipitate in the cold with the molybdic solution, but a yellow precipitate is formed if the solution be heated. H_4SiO_4 gives no reaction in the cold with molybdic reagents, and only a yellow coloration, but no precipitate, after heating the solution. The production of a mere yellow coloration is, by the molybdic reagent, therefore, no indication of phosphoric acid.

429. The properties of the phosphates of Fe, Cr, Al, and of metals of the alkaline earths, and other methods for detecting PO_4, are given in pars. 183, 184, 185, 186, 187, and 188.

430. As arsenic acid gives precipitates with $MgSO_4$, with ferric salts and with molybdic acid similar to those given by phosphoric acid, the arsenic acid, when present, must be removed, either by reducing it by SO_2 or by H_2S.

431. P may easily be detected in its compounds, even when they are mixed with large quantities of other substances, as follows:

(*a*) The sample, having been ignited, is rubbed fine on the porcelain plate (see fig. 3 in Plate), and is then introduced into a small glass tube of the thickness of a straw; into this tube, which is closed at the bottom, a piece of magnesium wire, about one fourth of an inch in length, is placed so that it is covered by the powder. On heating the tube, magnesic phosphide is formed with incandescence. The black contents of the tube powdered on the plate give, on moistening with H_2O, the highly characteristic smell of H_3P. A piece of Na can be equally well used if the Mg wire cannot be procured.

(*b*) If it has been ascertained that the sample does not yield any film on porcelain in the upper oxidizing flame, the phosphates may be recognised by heating on platinum with borax and a thin piece of iron wire in the hottest part of the reducing flame, when a bright molten bead of iron phosphide is obtained, which can be extracted with the magnetized knife on crushing the bead under paper.—*Bunsen*.

PYROPHOSPHORIC ACID, $H_4P_2O_7$.

432. This acid may be obtained by exposing orthophosphoric acid to a temperature of 215° C.; it appears under the form of a soft glass; it is converted into orthophosphoric acid by boiling it in water, and it is converted into metaphosphoric acid when heated to redness. The acid is also converted into orthophosphoric acid on boiling solutions of its salts with strong acids.

433. The free acid does not give precipitates with $BaCl_2$ and $AgNO_3$, but its salts give white precipitates with them.

434. White of egg is not precipitated by a solution of the acid, nor by solutions of its salts mixed with acetic acid. Ammonic molybdate, with addition of NH_4HO, fails to produce a precipitate.

METAPHOSPHORIC ACID, HPO_3.

435. This acid is obtained by acting on P_2O_5 with cold water, or by heating $H_4P_2O_7$ or H_3PO_4 to redness; it forms a transparent, colourless, glassy, uncrystallizable mass.

436. The solution of the acid gives precipitates with white of egg, with $AgNO_3$ and $BaCl_2$. It gives no precipitate or coloration with ammonic molybdate.

437. The metaphosphates do not coagulate the albumen of white of egg unless acetic acid be added, which liberates HPO_3. This is its most characteristic test.

438. This acid is converted slowly at ordinary temperatures, quickly at the boiling heat, into H_3PO_4.

CARBONIC ACID, H_2CO_3.

Solution for the reactions, Na_2CO_3 *in water*.

439. H_2CO_3 is supposed to be formed when CO_2 is passed into H_2O, but it has never been obtained; if it exists it decomposes when its solution is evaporated. CARBONIC ANHYDRIDE, CO_2, exists at the common temperature and pressure as a colourless, inodorous, and non-inflammable gas. Being heavier than the atmosphere in the proportion of 1·5 to 1, it can be decanted from one vessel to another like a liquid. It reddens blue litmus paper previously moistened with water, which after a time returns to its original colour, owing to the CO_2 having volatilized. It is soluble in cold water, but when the solution is heated it escapes.

440. As H_2CO_3 is bibasic, it forms with the monatomic metals two classes of salts, viz. neutral or normal salts, M'_2CO_3, and acid salts, $M'HCO_3$; the neutral and acid salts of the metals of the alkalies are alkaline to test-paper. The neutral alkaline carbonates are the only *neutral* salts of this acid which are soluble in water. The carbonates are decomposed by all free acids soluble in water (HCy and H_2S excepted), with evolution of CO_2.

441. *To detect* CO_2, add to the solution or solid substance under examination HCl, and warm the solution, if sufficient gas for detection cannot be procured without. Should any gas be evolved, allow it to accumulate by placing the thumb on the mouth of the test-tube, and afterwards decant it (taking care not to allow any of the liquid to pass over along with it) into another test-tube half filled with *lime-water*. A white precipitate of $CaCO_3$ will be produced if CO_2 is present.

442. When the solution under examination contains only a minute quantity of a carbonate, it is sometimes a matter of difficulty, especially to young students, to decant the CO_2 into the test-tube containing the lime-water; this is especially the case if the solution contains Na_2HPO_4, as CO_2 is very soluble in a solution of that salt. In such cases it would be better first to precipitate the CO_2 in conjunction with CaO or BaO, by

adding to the solution under examination a solution of $CaCl_2$ or $BaCl_2$, collecting the precipitate produced upon a filter, and after all the fluid has filtered off to transfer the precipitate again to the test-tube, moisten with water, then add HCl, and if any effervescence takes place to collect the gas in lime-water in the manner just described (441).

443. $CaCl_2$ and $BaCl_2$ produce in solutions of the neutral alkaline carbonates an *immediate* precipitate of $CaCO_3$ or of $BaCO_3$; but these chlorides in dilute solutions of the acid carbonates ($M'HCO_3$) form precipitates only after *ebullition;* in solutions of the free acid these reagents produce no precipitates.

444. Many of the insoluble carbonates dissolve in water containing CO_2, from which solutions they are precipitated on boiling, because the CO_2 is expelled. It is in this state that most of the Ca and Mg in spring and river water exists. The incrustations which are formed in the vessels in which such waters are boiled are due to the precipitation of these carbonates occasioned by the expulsion of the CO_2. The CO_2 in waters is best detected by adding to them *lime-water;* by this means not only is the $CaCO_3$ which is formed precipitated, but also that which pre-existed in the solution. This process is employed on the large scale for softening hard waters (waters containing in solution calcic and magnesic salts). It is called, after the inventor, Clarke's process.

445. All the carbonates, with the exception of those of the alkalies, lose their acid upon ignition, the metal being left either in an oxidized or uncombined state, according to its greater or less affinity for oxygen.

446. *The following precautions must be attended to in testing for this acid:*—When the substance is in the solid state it should be reduced to fine powder, and a little water should be added prior to the acid, to displace the air in its pores, otherwise an apparent effervescence will ensue from the expulsion of air. In the case of alkaline carbonates the decomposing acid must be added until the solution reddens blue litmus paper—that is, until the acid is in *excess;* otherwise the carbonic acid set free may combine with some of the un-

decomposed carbonate, forming with it an acid carbonate, no effervescence consequently taking place. No decomposition takes place on the addition of strong HNO_3 to $BaCO_3$, especially the native carbonate, because $Ba(NO_3)_2$ is insoluble in the strong acid. Water must therefore be added, as well as the acid, for the decomposition to be effected in this and many other cases.

OXALIC ACID, $H_2C_2O_4 = H_2\bar{O}$.

Solution for the reactions, $(NH_4)_2\bar{O}$ *in water.*

447. $H_2\bar{O}$ crystallizes from its aqueous solutions in four-sided prisms, which contain 2 ats. of water. The acid is very soluble in water and alcohol; its solution is very acid and poisonous. The crystallized acid melts at about 98° C. in its water of crystallization. The dry acid sublimes at 165° in slender white needles; part of it is, however, decomposed, and larger portions of it at an increased temperature, into CO_2 and formic acid, $HCHO_2$, the latter being resolved into carbonic oxide, CO, and H_2O. Heated with an excess of alkali, a carbonate is formed and H evolved. Cl does not act on dry $H_2C_2O_4$, but in presence of moisture it quickly decomposes it, thus:—$H_2C_2O_4 + Cl_2 = 2CO_2 + 2HCl$. $H_2\bar{O}$ may be crystallized from hot HNO_3, but by long-continued boiling in HNO_3 it is slowly oxidized, CO_2 and H_2O being formed. OXALIC ANHYDRIDE, C_2O_3, has not been obtained. When $H_2C_2O_4$ is dehydrated by concentrated H_2SO_4, H_3PO_4, or other dehydrating substances, the C_2O_3 splits up at the same time into CO_2 and CO.

448. $H_2C_2O_4$, like other bibasic acids, forms, with the monatomic metals, two classes of salts, viz. *neutral salts*, $M'_2C_2O_4$, and *acid salts*, $M'HC_2O_4$; but it also forms a third group of super-acid salts, $KH_32C_2O_4$. The oxalates of the alkaline metals are soluble in water; the rest are almost all insoluble in water, but soluble in dilute acids. All the oxalates are decomposed by heat. The oxalates of the more easily reducible metals, as Ag, Hg, Cu, give off CO_2, the metal

being left in the metallic state; the oxalates of the less reducible metals, whose carbonates are decomposed by heat, as Zn, Mg, &c., give off CO_2 and CO, the metal being left as oxide. The oxalates of the metals whose carbonates are not decomposed by heat, as K and Na, or not easily decomposed, as Ba, Sr, and Ca, give off CO, the metal being left as carbonate.

449. The *acid* or oxalates, heated with concentrated H_2SO_4, give off, with effervescence, CO_2 and CO, and if a light be applied to these gases as they issue from the mouth of the test-tube the CO will burn with a *blue* flame.

450. The acid or *oxalates*, on being mixed with some finely powdered MnO_2 (which must be free from carbonates), a little H_2O added, and a few drops of concentrated H_2SO_4, considerable effervescence ensues, owing to the CO_2 which is formed thus:—$MnO_2 + K_2C_2O_4 + 2H_2SO_4 = Mn''SO_4 + K_2SO_4 + 2H_2O + 2CO_2$. This reaction is employed for estimating the amount of MnO_2 in manganese ore (par. 127).

451. The soluble calcic salts and lime-water produce, even in highly dilute *solutions* of oxalates, a white precipitate of $Ca\bar{O}$, which is insoluble in acetic acid.

SILICIC ACID OR ORTHOSILICIC ACID, H_4SiO_4.

452. H_4SiO_4 may be obtained by passing silicic fluoride into water:

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6;$$

it may also be obtained by passing CO_2 into a solution of a soluble silicate:

$$Na_4SiO_4 + 4H_2O + 4CO_2 = H_4SiO_4 + 4NaHCO_3;$$

or by treating a solution of a soluble silicate with HCl. The H_4SiO_4, obtained in decomposing solutions of the alkaline silicates with acids, separates from the solutions in the form of a gelatinous mass, which is nearly insoluble in water and acids; but if a dilute solution of the silicate be poured into a considerable excess of HCl the H_4SiO_4 remains in solution, but is precipitated on neutralizing the solution with an alkali.

If the solution of the H_4SiO_4 is placed in one of Graham's dialysers, and the water in the outer vessel is changed every twenty-four hours, in four or five days the alkaline chloride and the excess of HCl have diffused so completely that the liquid in the dialyser contains not even a trace of them, but is a pure solution of H_4SiO_4, containing about 5 per cent. of the acid; the solution may be concentrated in a flask until it contains 14 per cent. of the acid; this solution is tasteless, limpid, colourless, and feebly acid: in a few days it becomes converted into a solid, transparent, jelly-like mass, which shrinks and gives up water even in closed vessels; the coagulation is retarded by HCl and by small quantities of KHO or NaHO. By evaporating this pure solution of H_4SiO_4 at 15·5° C., in a vacuum a transparent, glassy, very lustrous mass is left, which, after drying over H_2SO_4, yields DIBASIC SILICIC ACID, H_2SiO_3; in addition to these two there is evidence of other silicic acids. SILICIC ANHYDRIDE, SiO_2, is obtained on igniting H_4SiO_4 or H_2SiO_3 as a gritty white powder; it occurs in nature in two forms, the crystalline and amorphous; *rock crystal*, *quartz*, *amethyst* (coloured purple by ferric oxide) are pure, or nearly pure, crystallized SiO_2; *agate* and *chalcedony* consist of a mixture of crystallized and amorphous SiO_2; *opal* consists of the amorphous form with a varying quantity of water. Silica is the principal constituent of sandstones; it is also one of the constituents of felspar and of numerous other minerals. All the artificial forms of SiO_2 are amorphous. SiO_2, whether natural or artificial, is insoluble in water and all acids except HF, and it requires for its fusion a heat as intense as that of the oxyhydrogen blowpipe; at that temperature it melts to a transparent glass and is amorphous. H_4SiO_4 and amorphous SiO_2 dissolve in hot aqueous solutions of the fixed and carbonated alkalies; but the crystalline SiO_2 is dissolved by these reagents with far greater difficulty and in much less quantity, and it is also much more slowly attacked by HF. The amorphous and crystallized SiO_2, on being fused with alkaline carbonates, are converted into alkaline silicates, which are decomposed by acids, H_4SiO_4 separating. At common temperatures the silicic acids are weak acids, but at a red heat they expel H_2SO_4 and the more volatile acids from their salts.

453. "The composition of the SILICATES presents many varieties; some correspond to H_4SiO_4, for example Mg''_2SiO_4; others, such as Na_2SiO_3, correspond to the bibasic acid H_2SiO_3, and there are also the following among other silicates, $K_2Si_2O_5$, $Na_2Si_3O_7$, $Na_2Si_4O_9$." The alkaline silicates are the only silicates soluble in water; their solutions are alkaline to test-paper, and they are decomposed in solution by all acids; on evaporating their solutions to dryness along with a slight excess of HCl or HNO_3, and igniting the residue for some little time and then treating it with dilute HCl or HNO_3, the other substances dissolve, whilst the whole of the SiO_2 remains undissolved as a whitish gritty powder. On adding NH_4Cl to a concentrated solution of an alkaline silicate, a gelatinous precipitate separates.

454. Some of the silicates insoluble in H_2O are dissolved with decomposition by HCl or HNO_3; some that are not decomposed by these acids are decomposed by concentrated H_2SO_4. The silicates which are not acted upon by any acids but HF are decomposed by fusion with the alkaline carbonates, and also with BaH_2O_2.

455. The silicates decomposable by HCl or HNO_3 ought to be reduced to the finest powder, and be digested in the acid for some time at a gentle heat, with constant stirring, when the decomposition is effected; the mixture must be evaporated to dryness on the water-bath and the residue heated until acid fumes cease to be evolved; the dry mass is then moistened with HCl and heated with water, and then filtered; the filtrate must be examined for the bases and other acids, and the insoluble portion for SiO_2.

456. HF and SiO_2 mutually decompose each other, gaseous SiF_4 and H_2O being formed; silicates are converted by HF into silico-fluorides; $M''SiF_6$ and these salts, on being heated with H_2SO_4, are converted into sulphates, HF and SiF_4 being evolved. The silicates undecomposable by other acids are

decomposed by HF, but the fusion process is better suited for qualitative purposes.

457. Silicates not decomposed by acids must be reduced to the finest powder, and then intimately mixed with a mixture of Na_2CO_3 and K_2CO_3, and the mixed mass fused in a platinum crucible until the evolution of CO_2 *ceases*. The crucible, when cold, is put into an evaporating dish containing dilute HCl. When the fused mass is detached from the crucible, remove the crucible and evaporate the mixture to dryness, and ignite just in the same way as the solution in 455 is directed to be treated. The fixed alkalies cannot, of course, be sought for in that portion which has been fused with the alkaline carbonate; to ascertain whether they are present, another portion of the silicate must be fused with BaH_2O_2. For this purpose "mix one part of the very finely pulverized substance with four parts of BaH_2O_2; expose the mixture for half an hour, in a platinum crucible, to strong heat, and then treat the fused or agglutinated mass with HCl and water until it is dissolved. Precipitate the Ba and all the bases in the silicate, with the exception of Mg and the alkalies, with NH_4HO and $(NH_4)_2CO_3$; filter, evaporate to dryness, ignite, dissolve the residue in water, precipitate again with NH_4HO and $(NH_4)_2CO_3$, filter, evaporate, ignite;" then test for K and Na in the usual way.

458. When SiO_2 or H_4SiO_4 is fused with Na_2CO_3 before the blowpipe, a transparent colourless bead is formed, the CO_2 being expelled. A small quantity of Na_2CO_3 ought only to be employed, as an opaque bead is produced when it is added in excess.

HYDROFLUORIC ACID, HF.

459. This acid is best obtained by the action of concentrated H_2SO_4 on CaF_2, fluor spar. The powdered mineral is gently heated with the acid in a retort of lead, and the HF condensed in a receiver of the same metal. It is obtained in the form of a very volatile liquid, strongly acid and corrosive, fuming in the

air. It burns the skin like red-hot iron, causing a sore which is not easily healed. It is distinguished from all other acids by dissolving SiO_2 and the silicates which are insoluble in the other acids; on this account it cannot be prepared or kept in glass vessels.

460. "If a finely pulverized fluoride, no matter whether soluble or insoluble, is heated in a platinum crucible with concentrated H_2SO_4, the crucible covered with the convex face of a watch-glass, coated on that side with bees'-wax, which has been removed again in some places by tracing lines in it with some pointed instrument,* the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines will, upon the removal of the wax, be found etched into the glass. If the quantity of HF disengaged by the H_2SO_4 is very minute, the etching is often invisible upon the removal of the wax; it will, however, in such cases reappear when the plate is breathed upon. This appearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess." This method cannot be adopted if the substance containing the F is not decomposed by H_2SO_4, or if *silicic* acid is present; the silicic acid must be got rid of, in the way to be described, before we can discover F.

461. If nascent HF meet with SiO_2, we have seen they are mutually decomposed (par. 456). Should the substance examined contain, therefore, SiO_2 as well as F, SiF_4, and not HF, will be disengaged by the H_2SO_4. SiF_4 in the pure state is a colourless gas, which has a suffocating acid smell, and which emits fumes in contact with the air; it reacts with water, and forms H_4SiO_4, which is deposited in the gelatinous state, and H_2SiF_6, hydrofluosilicic acid, which remains in solu-

---

* The coating with the wax may be readily effected by heating the glass cautiously, putting a bit of wax upon the convex face, and spreading the fused mass equally over it. The instrument used for tracing the exposed lines should not be too hard; a pointed piece of wood answers best. The removal of the wax coating is effected by heating the glass gently and wiping the wax off with a cloth.

tion. SiF_4 does not attack glass; but the glass becomes covered, when damp, with a very adhesive coating of H_4SiO_4, which impairs its transparency, owing to the decomposition of the H_2O and SiF_4. H_2SiF_6 combines with the metallic oxides, and forms with them a class of salts called silicofluorides, which are decomposed by excess of alkali, SiO_2 being precipitated, and an alkaline fluoride remaining in solution.

462. To detect F in silicated fluorides which are *decomposable by* H_2SO_4, boil the substance with concentrated H_2SO_4 in a flask, retort, or test-tube, to which is attached a bent tube; conduct the evolved SiF_4 into a solution of NH_4HO; NH_4F and SiO_2 will be formed; heat, filter, evaporate in a platinum crucible to dryness, and examine the residue by the method described in 460. If the substance under examination contains only a slight trace of F and no other volatile acid, it is better to add a very little marble to the substance, so as to ensure a continuous slight evolution of gas. When the H_2SO_4 boils, all the SiF_4 is given off.

463. "Compounds not decomposable by H_2SO_4 must first be fused with four parts of Na_2CO_3 and K_2CO_3. The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum or silver vessel, HCl added to feebly acid reaction, and the fluid let stand until the CO_2 has escaped. It is then supersaturated with NH_4HO, heated, filtered into a bottle, $CaCl_2$ added to the still hot fluid, the bottle closed, and allowed to stand at rest. If a precipitate (CaF_2) separates after some time, it is collected on a filter, dried, and examined by the method described in 460."—*H. Rose.*

464. If a fluoride mixed with $KHSO_4$ is heated in a test-tube, HF is disengaged, which is easily detected by the etching of the glass. Consult also pars. 679 and 671, *9th b.*

HYDROSULPHURIC ACID (*Sulphuretted Hydrogen*, H_2S).

465. This acid exists at the common temperature and pressure as a colourless inflammable gas, possessing a highly offensive odour resembling that of rotten eggs. It burns with

a blue flame, the products of combustion being SO_2 and H_2O. It is soluble in water, three volumes of which dissolve one volume of the gas; this solution reddens litmus paper. On exposing the gas in a state of solution to the air, it is decomposed, H_2O being formed, and S being separated.

466. The sulphides of the metals of the alkalies and alkaline earths are the only metallic sulphides which are soluble in water; we have seen that these metals of the alkalies and alkaline earths form also sulph-hydrates and polysulphides, and these, as well as the monosulphides, are soluble in water, and their solutions are also alkaline to test-paper. The sulph-hydrates are distinguished from the sulphides by evolving H_2S on being decomposed by a metallic salt:—$2KHS + MnSO_4 = K_2SO_4 + MnS + H_2S$; and the polysulphides are distinguished from the sulphides and sulph-hydrates in that a separation of sulphur, as well as an evolution of H_2S, attends their decomposition by acids.

467. The colour of the insoluble metallic suphides and their behaviour with acids and other reagents have been noticed in the basic groups.

468. The sulphides soluble in water and the sulphides which are decomposed by HCl evolve H_2S on being treated with HCl, which, from its characteristic smell, is easily recognised. When the quantity is so minute that the smell fails to afford a sufficient proof, it may be detected by holding a piece of paper moistened with a solution of any soluble LEAD SALT over the mouth of the test-tube, as a brown or black coating of PbS will be formed upon the paper. To detect a trace of an alkaline sulphide in the presence of a free alkali or alkaline carbonate, add to the solution a solution of PbO in NaHO, which may be prepared by adding to a solution of $Pb\bar{A}_2$ one of NaHO until the solution which first forms is redissolved.

469. Sulphides which are not readily acted on by dilute HCl alone are readily acted on and evolve abundance of H_2S on the addition of a piece of Zn.

470. When sulphides are dissolved in HNO_3 or aqua regia, H_2SO_4 is formed along with a separation of S. In the case of

sulphides, therefore, which, from their insolubility in HCl, must be dissolved in HNO_3 or aqua regia, the sulphur is converted into H_2SO_4, and not given off as H_2S.

471. To ascertain whether the S existed in an unoxidized state, when HNO_3 or aqua regia has been employed as the solvent of the substance under examination, a small portion of the *original* substance, in fine powder, must be fused with a little solid KHO or NaHO, in a platinum spoon, by means of the blowpipe flame. The fused mass must then be dissolved in a little water and filtered; a bright strip of silver (or polished coin) is put into the solution, and the fluid warmed. If a sulphide were present, a brownish-black film of Ag_2S will form upon the metal. This film may be removed afterwards by rubbing the metal with leather and CaO. For other methods of detecting sulphides, see pars. 671, *7th;* 673, *d;* 675 and 678.

HYDROCHLORIC ACID, HCl.

Solution for the reactions, NaCl *in water.*

472. This acid is a transparent and colourless gas, of a pungent, acrid, suffocating smell, and fuming strongly in moist air. It is absorbed in large proportion by water, forming the common liquid HCl, which is a mere solution of the gas in water. With the exception of AgCl and HgCl, all the neutral metallic chlorides are soluble in water; the solutions of the chlorides of the metals of the alkalies and alkaline earths and of Mn are neutral to test-paper.

473. When a chloride is heated with MnO_2 and H_2SO_4, Cl is evolved, which may be recognised by its ODOUR and GREENISH-YELLOW COLOUR.

474. When a chloride in the solid state and dry is heated with K_2CrO_4 in the solid state and *concentrated* H_2SO_4, a brown gas is disengaged, which condenses into a blood-red liquid, CHLOROCHROMIC ACID, CrO_2Cl_2. On the addition of NH_4HO in excess, the colour changes to a yellow, owing to the formation of $(NH_4)_2CrO_4$; upon the addition of an acid, the

yellow changes to a reddish-yellow colour, owing to the formation of $(NH_4)_2Cr_2O_7$.

475. If in a bead of $NaNH_4HPO_4$ on a platinum wire, CuO be dissolved in the outer blowpipe flame in sufficient quantity to make the mass nearly opaque, a trace of substance containing Cl added to it while still in fusion, and the bead then exposed to the reducing flame, a fine BLUE-COLOURED flame, inclining to PURPLE, will be seen encircling it so long as Cl is present.—*Berzelius.*

476. Free Cl may be readily detected in a solution by adding some of the fluid to a solution containing a ferrous salt and a sulphocyanide; the solution turns red by reason of the Cl converting the ferrous into a ferric salt; it may also be detected in the absence of nitrous acid, by adding the solution to one of KI and starch paste, when a blue colour will be instantly produced.

HYDRIODIC ACID, HI.

Solution for the reactions, KI *in water.*

477. HI and the iodides resemble in their properties the corresponding compounds of Cl and Br. HI is gaseous; it is extremely soluble in water, and the solution, which is colourless, resembles in properties that of HCl and HBr; but it is more easily decomposed than the two latter compounds by substances which have an affinity for H, and also by those substances which have an affinity for the other constituent. The colourless solution turns speedily to a reddish-brown when in contact with the air, owing to the formation of H_2O and the liberation of I, which is dissolved by the undecomposed HI. HI and the iodides are decomposed by Cl and by Br, owing to these two elements having a greater affinity for H and the metals. HI, in the gaseous state, may be obtained by placing in a small retort 10 parts of KI with 5 of H_2O and 20 of I, then drop in cautiously 1 part of P in small pieces, and apply a gentle heat; the following equation explains the reaction:—$4KI + 5I_2 + P_2 + 8H_2O = 2K_2HPO_4 +$

14HI. HI in solution is easily prepared by suspending I in water and passing H_2S through the mixture; HI is formed, and S is set free. "The iodides, as a rule, are less volatile, more insoluble, and more easily decomposed, than the chlorides and bromides. The iodides of Sn, Sb, and As, like the chlorides and bromides, are decomposed by H_2O. The hydrated iodides of Mg, Zn, and Al are, like the chlorides and bromides, decomposed by heat into metallic oxide and HI. In addition to the iodides of Pd, Pt, and Au, AgI, unlike the chloride and bromide of Ag, is decomposed at a red heat. All iodides, except those of the alkali- and alkaline-earth groups, are decomposed at a red heat by a current of H. The iodides, with the exception of those last mentioned, and those of Pb and Bi, are also decomposed by O at a red heat."

478. $HgNO_3$ throws down from solutions of the iodides a yellowish-green precipitate of HgI.

479. $HgCl_2$ throws down a red precipitate of HgI_2, which is soluble in an excess of the $HgCl_2$ or of KI.

480. *Soluble lead salts* precipitate an orange-yellow of PbI_2.

481. Free I forms with *starch*, even in highly dilute solutions, a compound of a deep *blue colour*. If the I is in a state of combination with H or any metal, it is necessary to liberate it before applying the starch test; the blue compound is decolorised at a temperature of 70° or 80° C., but recovers its colour as the liquid cools; it is decomposed by Cl, Br, and the alkalies.

482. Cl liberates I from its combinations; if added in excess, they combine, forming colourless ICl_3.

483. If iodides are heated with H_2SO_4 and MnO_2, the I sublimes in the form of violet-coloured vapours, which are easily recognised; this process is the one followed in the manufactory for obtaining the iodine from the kelp liquors.

484. Palladious chloride, $PdCl_2$, produces even in very dilute solutions of HI and of metallic iodides a brownish-black precipitate of PdI_2, which is insoluble or nearly so in cold dilute HCl and HNO_3. $PdCl_2$ does not precipitate Br from its solutions.

485. Pure HNO_3, free from nitrous acid, decomposes HI or iodides only when acting upon them in its concentrated form, particularly when aided by the application of heat. But HNO_2 and *peroxide of nitrogen*, N_2O_4, decompose HI and iodides with the greatest facility even in the most dilute solutions. Colourless solutions of iodides, therefore, acquire immediately a brownish-red colour upon the addition of some red fuming HNO_3, or of a mixture of this with concentrated H_2SO_4, or, better still, upon addition of a solution of N_2O_4 in H_2SO_4, or of nitrite of potash and some H_2SO_4 or HCl. From more concentrated solutions the I separates under these circumstances in the form of small black plates or scales, whilst nitric oxide gas, NO, and iodine vapour escape.

486. The best method of detecting I in a solution is to mix with the liquid a little starch paste, and acidify it with HCl. A solution of KNO_2* is then to be added, when, if much I be present, a dark blue colour will be instantly produced; if a very small quantity only—as, for instance, the two or three millionth part—then a few seconds elapse before the blue colour makes its appearance.

487. When a solution containing 1 part of $CuSO_4$ and 2½ parts of $FeSO_4$ is added to a neutral or slightly alkaline solution of an iodide, a white precipitate of cuprous iodide, CuI, is formed. The $FeSO_4$ is added, to convert the $Cu''SO_4$ into Cu'_2SO_4. The addition of a small quantity of a solution of Na_2CO_3, so as to render the solution slightly alkaline, promotes the complete precipitation of the I. Chlorides and bromides are not precipitated by this reagent.

488. A bead of $NaNH_4HPO_4$ saturated with CuO, if mixed with a substance containing I, and ignited in the inner blowpipe flame, imparts an intense GREEN COLOUR to the flame.

---

* A solution of N_2O_4 in H_2SO_4 may be employed in place of the KNO_2 and HCl. Fresenius states that a single drop on a glass rod of the N_2O_4 solution suffices to produce the reaction most distinctly.

IODIC ACID, HIO_3.

489. This acid is a white crystalline solid; it is decomposed at a moderate heat into O and I; it is readily soluble in water. Its salts are decomposed by heat, a metallic iodide and free oxygen being formed, or into iodine, oxygen, and a metallic oxide; the alkaline iodates are the only salts of this acid which dissolve readily in water. $AgNO_3$ and $BaCl_2$ precipitate it from its solutions.

490. SO_2 and H_2S each throw down I from solutions of HIO_3; if an excess of either reagent is added, the I becomes converted into HI.

491. An iodate can be detected in the presence of an iodide by the simple addition of a strong acid; the HI and HIO_3 act upon each other in the following manner:—$5HI + HIO_3 = 3I_2 + 3H_2O$.

HYDROBROMIC ACID, HBr.

Solution for the reactions, KBr *in water.*

492. Br at the ordinary temperature is a liquid of a deep red colour; it is soluble in water, but it is much more soluble in alcohol, ether, chloroform, and bisulphide of carbon; the solutions are reddish-yellow. Br, especially in its vaporous state, turns moistened starch yellow; the yellow colour does not always appear instantaneously. HBr is a gas which closely resembles in its properties HCl gas. It emits in the air white fumes, which are denser than those produced by HCl; it is decomposed by Cl, Br being set free, and HCl formed; the liberated Br appears under the form of reddish vapours, or condenses into reddish drops. HBr is extremely soluble in H_2O; the solution is colourless, unless it contains free Br, which it dissolves in large quantities; it has then a dark reddish colour. HBr, in the gaseous state, may be obtained by heating KBr with H_3PO_4, or by acting on PBr_3 with water, HBr and phosphorous acid, H_3PO_3, being formed. It may be obtained in solution by passing H_2S through water which contains Br. The bromides are solid at ordinary temperatures; most of

them are fused by a moderate heat and are partially volatilized; the bromides of Au and Pt are decomposed by heat; most of the bromides are readily soluble in water.

493. HBr and the bromides, with the exception of AgBr and HgBr, are decomposed by HNO_3, on the application of heat, the H or the metal being oxidized and the Br liberated; if the bromide operated upon is in the solid state or as a concentrated solution, the Br vaporizes; but if the bromide is in a state of solution and not very concentrated, the Br dissolves in the liquid, colouring it yellow or yellowish-red. In the cold, HNO_3, even the fuming red acid, does not liberate Br from moderately dilute solutions of the bromides, nor is it liberated by a solution of N_2O_4 in HCl, or by H_2SO_4 and KNO_2.

494. Cl, in the *gaseous state* or in *solution*, immediately liberates Br in the solutions of its compounds; the fluid assuming a yellowish-red tint if the quantity of Br present is not too minute. A large excess of Cl must be avoided, since this will cause the formation of chloride of bromine, which will destroy the colour wholly or nearly so. This reaction is made much more delicate by addition of a fluid which dissolves Br and does not mix with water, as sulphide of carbon or chloroform. Mix the neutral or feebly acid solution in a test-tube with a little of one of these fluids, sufficient to form a large drop at the bottom, then add dilute chlorine-water drop by drop, and shake the tube. With appreciable quantities of Br, for example 1 part in 1000 parts of water, the drop at the bottom acquires a reddish-yellow tint. A large excess of chlorine-water must be avoided, and it must always be first ascertained whether, when mixed with a large quantity of water and some sulphide of carbon or chloroform, and shaken, it leaves these reagents quite uncoloured; if it does not, it ought not to be employed. If the solution of Br in sulphide of carbon or chloroform is mixed with a solution of KHO, the mixture shaken, and heat applied, the yellow colour will disappear, KBr and potassic bromate, $KBrO_3$, being formed. By evaporating this solution to dryness and igniting the

residue, the $KBrO_3$ will be converted into KBr. On heating the bromide with MnO_2 and H_2SO_4 in a small retort YELLOWISH-RED VAPOURS will be evolved unless the quantity be very minute. These vapours, when brought in contact with *starch paste*, will communicate to it an ORANGE-YELLOW COLOUR, which disappears on exposure to the air.*

495. Br in presence of I and Cl may be identified by the following simple operation:—Mix the fluid with a few drops of dilute H_2SO_4, then with some starch paste, and add a little red fuming HNO_3, or, better still, a solution of N_2O_4 in H_2SO_4, whereupon the iodine reaction will show itself immediately. Add now chlorine-water drop by drop until that reaction has disappeared, then add some more chlorine-water to set the Br also free, which may then be separated and identified by means of chloroform or bisulphide of carbon, or the liberated I may also be taken up with chloroform or bisulphide of carbon, and chlorine-water cautiously added, when the violet-red coloration imparted by the iodine gradually fades away, and after its disappearance the brownish-yellow colour given by the Br is distinctly visible. (*Fresenius.*)

496. Solid bromides, when distilled with $K_2Cr_2O_7$ and CONCENTRATED H_2SO_4, yield pure Br, which becomes colourless, or nearly so, when treated with excess of NH_4HO; by this means it is distinguished from chlorochromic acid, which it resembles in colour. (See par. 474.)

497. If a $NaNH_4HPO_4$ bead saturated with CuO is mixed with a substance containing Br, and then ignited in the inner blowpipe flame, the flame is coloured BLUE, inclining to GREEN, more particularly at the edges.—(*Berzelius.*)

---

* Fresenius recommends that the fluid containing the free Br, or the mixture of bromide, MnO_2, and H_2SO_4, be gently heated in a very small beaker, covered with a watch-glass with a slip of paper attached to the lower side, moistened with starch paste, and strewed over with starch powder; in the course of a short time, if bromine is present, a yellow tint will be imparted to the starch.

HYDROCYANIC ACID (*Prussic Acid*), HCN OR HCy.

Solution for the reactions, KCy *in water*.

498. In its anhydrous state HCy is a colourless, volatile, inflammable liquid, possessing a strong odour resembling oil of bitter almonds; it boils about 27° C., and evaporates in large quantities far below its boiling-point; a small quantity of the vapour is sufficient to produce instantaneous death. Water dissolves it in all proportions; the solution is liable to undergo decomposition if exposed to the light, the decomposition taking place more quickly as the acid is stronger; alkalies accelerate the decomposition, but the presence of a small quantity of HCl impedes decomposition; concentrated HCl, on the other hand, decomposes HCy immediately into NH_4Cl and $HCHO_2$ (formic acid); concentrated H_2SO_4 produces the same decomposition, but further converts the $HCHO_2$ into CO and H_2O. Although $HCHO_2$ is one of the products of decomposition of HCy, NH_4CHO_2 (ammonic formate) is converted by heat into HCy and H_2O; on boiling HCy with an excess of KHO, NH_3 is evolved and $KCHO_2$ remains in solution. "To prepare a solution of HCy the usual plan is to decompose in solution K_4FeCy_6 by dilute H_2SO_4, and distil; the best proportions are 10 parts of crystallized K_4FeCy_6 dissolved in 50 parts of H_2O; 3·5 parts of common H_2SO_4 are then mixed with 25 parts of H_2O, and the mixture, when cold, is poured into the solution of the salt, and then distilled; the equation explains the reaction:— $2K_4FeCy_6 + 3H_2SO_4 + Aq = 6HCy + K_2Fe_2Cy_6 + 3K_2SO_4 + Aq$." The solution of HCy is feebly acid to test-paper; it does not decompose the alkaline carbonates; it readily dissolves HgO, forming $HgCy_2$, and, when mixed with a solution of the alkalies, alkaline cyanides are formed, which are soluble in water; their solutions are alkaline to test-paper, and they are decomposed with the liberation of HCy by the weakest acid. $HgCy_2$ is soluble in water; most of the cyanides of the other heavy

metals are insoluble. Some of the cyanides give off HCy when treated with dilute solutions of the stronger mineral acids; others, as ferrous and aurous cyanides, may be boiled with moderately strong acids without decomposition. Most of the insoluble cyanides dissolve in solutions of the alkaline cyanides, forming double cyanides. KCy and NaCy sustain a red heat without decomposition, if air and moisture be excluded; heated in contact with the air, they are converted into cyanates, M'CyO, and when further heated into carbonates. AgCy and $HgCy_2$ on being heated give off Cy as gas; other cyanides give off N, a mixture or compound of C and the metal being left. All the cyanides, when heated in the presence of water, are destroyed; the alkaline cyanides are converted by continued boiling with water into NH_3 and alkaline formates.

499. If to a solution of HCy or an alkaline cyanide KHO and a mixed solution of a ferrous and ferric salt be added, a greenish-blue precipitate will be produced; on the addition of HCl *insoluble Prussian blue* separates. If only a very minute quantity of HCy is present, the fluid simply appears green after the addition of the HCl, and it is only after long standing that a trifling blue precipitate separates from it.*

500. "If to a solution of HCy KHO is added in excess, and then finely pulverized HgO, the latter dissolves as readily as it would in free HCy. Since HgO is soluble in solutions of the alkalies *only in presence of* HCy, this reaction may be looked upon as a positive test for that acid."—*Fresenius.*

501. When HCy is added to $(NH_4)_2S$ containing an excess of S ammonic sulphocyanide, NH_4CyS_2, is formed, which gives a *deep blood-red colour* with ferric salts (179). This test may be applied in qualitative analysis in the following way:—Add a few drops of *yellow* $(NH_4)_2S$ to the liquid supposed to con-

---

* This test may be modified by heating gently the suspected mixture with H_2SO_4, and suspending in the flask or retort, for a few minutes, a piece of paper moistened with a solution of KHO; on dropping a weak solution of the mixed iron salts upon the paper, and immersing it in diluted H_2SO_4, HCy may be recognised by the formation of Prussian blue when very minute traces only are present.—*Miller.*

tain the HCy; evaporate at a *gentle heat* (not above 100° C.), until the excess of $(NH_4)_2S$ has completely volatilized, which is ascertained by the smell; then test the solution with a drop or two of Fe_2Cl_6. This test is exceedingly delicate. "If an acetate is present, the reaction takes place only upon addition of HCl."—*Fresenius.*

502. By neither of the above methods will Cy be discovered in $HgCy_2$; the solution of $HgCy_2$ must be treated with H_2S, HgS will be precipitated, and HCy remain in solution; examine then for HCy according to pars. 499, or 501, or 503.

503. Schönbein has recently proposed a new and exceedingly delicate test for this acid; it consists of paper imbued with resin of guaiacum, and moistened with a solution of $CuSO_4$, in contact with this acid the prepared paper immediately assumes a *blue colour*. To employ this test a slip of the paper imbued with guaiacum is moistened with the solution of $CuSO_4$, and brought in contact with HCy, either dissolved in water or diffused in the air, when it immediately becomes blue; the colour developed on the paper remains for a long time, but diminishes as the paper dries. After several days it passes to a greenish-grey, but revives slightly on moistening the paper.

504. *Detection of the acid in organic mixtures.*—Place the suspected mixture in a wide-mouthed bottle. (1) Introduce into the atmosphere of the bottle Schönbein's paper. (2) Smear a glass plate with a drop of yellow ammonic sulphide, and place it over the mouth of the bottle; subsequently evaporate the excess of $(NH_4)_2S$ at a low temperature, and proceed as directed at par. 501. (3) Smear a glass plate with a mixture of KHO and $FeSO_4$, and place it over the mouth of the bottle for a few minutes, then acidify with HCl (par. 499). "In order to obtain the acid from the coats of the stomach or its contents, the substance, cut into small pieces, should be mixed with cold distilled water, and distilled by a water-bath at a low temperature (77° C.), the distillate being collected in a *cold* receiver; if the suspected liquid is alkaline, a small quantity of tartaric acid may be added to neutralize it;

the distillate may then be examined by the three preceding tests."

NITRIC ACID, HNO_3.

Solution for reactions, KNO_3 *in water.*

505. HNO_3, when pure, is a colourless liquid, boiling at 86° C. with partial decomposition, a weaker acid being left behind; it fumes strongly in the air, and absorbs water from it, but with less avidity than H_2SO_4. It is frequently of a yellowish or red colour, owing to the presence of some of the lower oxides of nitrogen. Owing to the facility with which it gives up oxygen, it is, especially when heated, a most powerful oxidizing agent; its action upon the metals has been already noticed, it acts more or less powerfully on all the solid non-metallic elements. It acts with great energy on most organic bodies, the kind of action, varying with the strength of the acid and the temperature; organic substances containing nitrogen are stained yellow by the acid. NITRIC ANHYDRIDE (N_2O_5) is a very unstable body.

506. All the neutral nitrates are soluble in water; a few of the basic salts are insoluble in that liquid, the solutions of the nitrates of the metals of the alkalies and alkaline earths, and of silver and manganese are neutral to test-paper. Most of the nitrates fuse readily when heated, they are all decomposed at an elevated temperature; "the nitrates of the highly basylous metals at first give off nearly pure O, and are converted into nitrites, afterwards a mixture of O and N, together with some nitric peroxide (N_2O_4). Other nitrates, which decompose at a lower temperature, those of Hg, Pb and Ag, for instance, evolve a mixture of N_2O_4 and O. A few still more easily decomposable hydrated salts, aluminic and bismuthic trinitrates, for instance, give off HNO_3. Ignited $AgNO_3$ leaves a residue of Ag, but most normal nitrates, when strongly heated, leave residues of oxides analogous in composition to the original salt, but ferrous and manganous nitrates leave oxides richer in

oxygen than those which correspond to the original salts, viz. Fe_2O_3 and Mn_3O_4. Nitrates heated with combustible bodies produce a more or less violent deflagration or explosion. The acid-forming bodies, metallic or non-metallic, when deflagrated with nitre, leave potassic or sodic salts of the respective acids."

507. To detect HNO_3 in a solution, add to it one fourth of its volume of undiluted H_2SO_4, and *gently warm* the solution; a solution of a ferrous salt must then be added, along with a few drops more of the H_2SO_4, when the liquid will become of a deep brown colour, attended, most likely, with an energetic disengagement of gas; the colour, in this case, will soon disappear, for a reason presently to be named, but can readily be reinstated by a fresh addition of the ferrous solution. Or the solution of the ferrous salt may be added first to the solution of the nitrate, and then the undiluted H_2SO_4 poured in, in such a way that it forms a layer at the bottom of the test-tube; in this case the deep-brown colour will be produced at the contact-surface of the two liquids. The dark brown colour is owing to the formation of a compound of nitric oxide (NO) and the ferrous salt, the formula of the compound being $2Fe''SO_4,NO$; this compound is destroyed by heat with the disengagement of the NO, hence the fading of the colour when the solution is heated.

508. When nitrates are heated with undiluted H_2SO_4, in the presence of *copper turnings*, NO is evolved, which, in contact with the air, forms red fumes, owing to its absorption of oxygen and its conversion into nitrous anhydride (N_2O_3) and nitric peroxide (N_2O_4). This experiment ought to be conducted in a narrow test-tube. The colour is best observed by looking into the test-tube lengthways.

509. The following is an exceedingly delicate test for detecting HNO_3, it is therefore specially adapted for detecting the acid in water. Dissolve brucin in 1000 times its weight of water, pour about 15 grains of this solution into a test-tube, then add a little of the water to be tested, and lastly some H_2SO_4; the acid is made to flow down the side of the tube so

as to gather beneath the water. At the place of contact of the two liquids a rose-red zone immediately forms, if HNO_3 be present in detectable quantity. The reagents must be specially purified before they can be employed. The water employed to dissolve and wash the brucin must be repeatedly rectified over KHO. The brucin is washed with the pure water several times to remove nitrates. The H_2SO_4 is mixed with 5 per cent. of NH_4HCO_3, and three fourths distilled off in a glass vessel. (*Kersten.*)

510. The following has recently been proposed as a delicate test for nitrates, and, therefore, specially applicable for their detection in water. Into a test-glass about 1 cub. cent. of pure concentrated H_2SO_4 is placed (sp. gr. 1·84), to this is added drop by drop ½ cub. cent. of a solution of sulphate of aniline prepared by adding 10 drops of aniline of commerce to 50 cub. cent. of dilute H_2SO_4 diluted in the proportion of 1 of acid to 6 of water. A glass rod is dipped into the liquid to be tested and then into the test-glass; on moving the stirrer about gently, when the slightest trace of HNO_3 is present, red streaks mark the course of the glass rod; when there is slightly more than the merest trace, the liquid becomes carmine tinted; and with a still further quantity a deep red tint, which turns reddish-brown. Hyponitric acid produces the same reaction.

511. Dissolve 1 part of carbolic acid (phenol) in 4 parts of concentrated H_2SO_4, and dilute the solution with 2 parts of water. If the substance to be examined for HNO_3 is in solution, evaporate it in a porcelain crucible or its cover, and let fall one or two drops of the phenyl-sulphuric acid solution upon the residue at a temperature of about 100° C. By the excess of the H_2SO_4 any nitrates, if present, will be decomposed, and the HNO_3 derived from them will directly form nitro-compounds with the phenol, which are indicated by the production of a reddish-brown colour. When neither organic matters, nor compounds of Cl, I, and Br, from which H_2SO_4 easily separates carbon or the haloids, are present, this coloration is in itself convincing. But for fear of their presence, it

is better, in all cases, to add a drop or two of strong NH_4HO to the coloured product, when the haloids will be dissolved in the form of colourless salts, and the carbon remain suspended in the small particles, not interfering with the recognition of the characteristic yellow solution of the nitro-phenylate of ammonia. Frequently, after the addition of NH_4HO, there appears instead of a yellow an unstable emerald-green colour, which changes into a rose colour after the addition of an acid, and occasionally becomes greenish-yellow. (*Sprengel.*)

512. When a minute quantity of *gold*-leaf is boiled in HCl, no action is produced; but on the addition of a little HNO_3, or a nitrate, the gold quickly disappears and may be detected in solution by the method described in par. 284.

513. When a moderately concentrated solution of KHO is poured upon a mixture of Zn and Fe, H is freely disengaged, even without the application of heat; if a nitrate is added to this mixture evolving the H, it is followed by an immediate development of ammonia. This reaction furnishes a good qualitative test of the presence of nitric or nitrous acid. The fluid to be examined is reduced to a small bulk, and poured into a test-tube containing two or three grammes of a mixture of granulated zinc and clean iron filings. A small quantity of strong KHO solution is added, and the whole heated to boiling. The usual tests for ammonia may be applied at the mouth of the tube. (*Harcourt.*)

514. Very minute quantities of HNO_3 may be detected by reducing it first to nitrous acid, which may be effected both in the moist and the dry way; in the former by treating the solution of the HNO_3 or of the nitrate for some time with finely divided zinc, best with zinc amalgam, and then filtering (*Schönbein*); in the dry way by fusing the substance under examination with Na_2CO_3 and K_2CO_3 at a moderate heat, exhausting the mass, after cooling, with water, and filtering. Upon adding either of the filtrates to a solution of KI, mixed with starch and dilute H_2SO_4, the fluid acquires a blue colour from iodide of starch; see pars. 485 and 486. (*Fresenius.*)

515. If a mixture of nitrate with KCN in powder is heated upon platinum foil, a violent deflagration will ensue, owing to the sudden evolution of CO_2 and N, produced by the oxidation of the CN. Very minute quantities of nitrates may be detected in this way.

NITROUS ACID, HNO_2.

516. Nitrites give a *brown colour* with ferrous salts without the addition of an acid. Acidulated solutions of nitrites produce at once a purple colour with starch and KI. The *nitrates* do not colour ferrous salts brown or decompose KI until the nitric acid has been liberated and reduced to nitrous acid by warming with sulphuric acid.

517. Nitrites are, like nitrates, oxidizing agents, but they act more readily than the latter. Nitrites act also as reducing agents, acidulated solutions decolourise potassic permanganate, and gradually change potassic bichromate to a greenish hue; they also reduce $AuCl_3$ and mercurous salts; these reducing actions distinguish them from nitrates.

CHLORIC ACID, $HClO_3$.

518. This acid, in its concentrated state, appears in the form of a yellow syrupy liquid, the odour of which resembles that of HNO_3; the dilute acid is colourless and inodorous. $HClO_3$ is an unstable acid, it gradually undergoes decomposition on exposure to light; at a temperature of 40° C. it undergoes decomposition, and at 100° C., or a little above, it is rapidly converted into perchloric acid ($HClO_4$), oxygen, chlorine, and water:—$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O$.

It is decomposed by contact with organic matter; it is a very powerful oxidizing and bleaching agent; it reddens litmus first and afterwards bleaches it. CHLORIC ANHYDRIDE has not been obtained.

519. All the chlorates are soluble in water; they are decomposed upon ignition, oxygen being given off, and generally the metal is left as a chloride; but in the case of magnesic and some other chlorates the metal is left as an oxide, Cl and O being given off:—$2MgClO_3 = 2MgO + Cl_2 + 2O_2$.

Fused chlorates are powerful oxidizing agents; when heated with organic substances, they deflagrate with far greater violence than the nitrates. The solutions of the chlorates of the metals of the alkalies and alkaline earths are neutral to test-paper.

520. To detect this acid, add to a small quantity of the solid substance under examination a few drops of *undiluted* H_2SO_4 in the cold. The chlorate will be decomposed, $KHSO_4$ and POTASSIC PERCHLORATE ($KClO_4$) being formed, along with a GREENISH-YELLOW COLOURED explosive gas, perchloric oxide (Cl_2O_4), which escapes:—$3KClO_3 + 2H_2SO_4 = KClO_4 + Cl_2O_4 + 2KHSO_4 + H_2O$, the application of heat must be avoided, and the quantities operated upon should be small, to prevent any loud and violent explosion taking place.

521. If the solution of a chlorate is coloured light blue, with some solution of indigo in sulphuric acid, a little dilute H_2SO_4 added, and a solution of sulphite of soda dropped cautiously into the blue fluid, the colour of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid of its oxygen, and the liberated chlorine decolorises the indigo. (*Fresenius.*) This test readily distinguishes chlorates from nitrates.

522. Upon heating chlorates with HCl the constituents of the two acids decompose, forming water, chlorine, and an oxide of chlorine. The test-tube in which the experiment is made becomes filled in this process with a greenish-yellow gas, of a very disagreeable odour, resembling that of chlorine; the HCl acquires a greenish-yellow colour.

523. If a mixture of chlorate and KCy is gently heated upon platinum foil, a very violent deflagration ensues, even with a minute quantity of chlorate. The experiment must only be made with very minute quantities of chlorate.

CLASSIFICATION OF THE INORGANIC ACIDS, INCLUDING OXALIC ACID, WITH A DESCRIPTION OF THE PROCESSES TO BE FOLLOWED IN THE EXAMINATION OF SUBSTANCES FOR THESE ACIDS.

524. *Classification of the acids.*—The inorganic acids described in this book may be conveniently divided into four groups, as follows:—

FIRST GROUP.

1st Division.—Acids which are precipitated by H_2S from acid solutions, as *sulphides*—ARSENIOUS and ARSENIC ACIDS. *2nd Division.*—Acid which is converted by H_2S into a *base*—CHROMIC ACID. The acids contained in this group are detected in testing for the bases. ARSENIOUS and ARSENIC ACIDS, being precipitated by H_2S, are classed amongst the bases; whilst CHROMIC ACID is converted into Cr_2O_3, a member of the fourth group of bases; the change of colour attending this conversion is so characteristic, that it cannot be overlooked by the most inexperienced student. The only thing which can cause the least difficulty or perplexity is the mistaking a green solution, with a light-coloured precipitate suspended in it, for a green precipitate.

SECOND GROUP.

525. *1st Division.*—Acids which are precipitated by $BaCl_2$, or any soluble baric salt from *neutral, but not from acid,* solutions, their baric salts being soluble in acids. The members of the 1st group, and likewise PHOSPHORIC, OXALIC, HYDROFLUORIC, BORACIC, SILICIC, and CARBONIC ACIDS.* *2nd Division.*—Acid

---

* Baric borate, also baric oxalate and fluoride, are soluble in solutions containing ammonic salts; the last two are soluble in a less degree than the baric borate. A borate, oxalate or fluoride may be present in a solutio which gives no precipitate on the addition of a soluble baric salt, if ammonic salts are present.

which is precipitated by $BaCl_2$, or any soluble baric salt from *acid*, as well as *neutral* solutions—SULPHURIC ACID.

(*a*) All these baric salts are *colourless*, with the exception of BARIC CHROMATE, which is of a *pale-yellow colour*. If arsenious, arsenic, or chromic acid has been detected in examining for the bases, it should be got rid of from the portion of the solution to which the baric and silver salts are to be added by *slightly* acidifying the solution with HNO_3, if it is not acid to test-paper, and treating it with an excess of H_2S, filtering if necessary, gently boiling the solution until the excess of H_2S is removed, and neutralizing it with NH_4HO. If CO_2 has been detected in testing for the bases, it is better to get rid of it also before adding the baric salt, by adding, as before, HNO_3 until it is slightly in excess, and then boiling for a short time; and, as before, neutralizing the solution with NH_4HO. To the *neutral* solution thus prepared, if one or all of these four acids were present, or to the *neutral* solution if they are not present, a solution of $BaCl_2$ is added, or if an argentic or mercurous compound is present, a solution of $Ba(NO_3)_2$; if no precipitate is formed the acids of this group, with the exception of those got rid of, are absent; * if a precipitate is produced add *dilute* HCl, or *dilute* HNO_3, if $Ba(NO_3)_2$† has been employed; if the whole of the precipitate, or a portion of it is dissolved, one or more of the acids whose baric salts are soluble in acids are present; if the whole or a portion of it is insoluble in acids, H_2SO_4 or a *sulphate is present.*

THIRD GROUP.

526. *1st Division.*—Acids which are precipitated from *neutral,*

---

* The absence of the acids whose baric salts are soluble in ammonic salts, if these are present, is not established by this experiment (see note, page 209).

† Concentrated HCl or HNO_3 must not be employed, because $BaCl_2$ and $Ba(NO_3)_2$ are insoluble in them, and would therefore separate from the solution.

but not from acid, solutions by $AgNO_3$. The members of the 1st and 2nd groups, with the exception of SULPHURIC ACID. *2nd Division.*—Acids which are precipitated from *acid* as well as *neutral* solutions—HYDROSULPHURIC, HYDROCHLORIC, HYDROBROMIC, and HYDRIODIC ACIDS. HC

The following silver salts are coloured:—ARGENTIC SULPHIDE, *black;* the CHROMATE *red;* the ARSENIATE *reddish-brown;* the ARSENITE, PHOSPHATE, and IODIDE, *yellow;* the SILICATE, *yellow* or *white;* the BROMIDE, *yellowish-white.* The silver salts of the rest of the acids of the group are colourless. Besides removing the acids of the 1st group and CO_2, it is necessary also to get rid of a sulphide before adding the *silver salt,* and as *ferrous sulphate* reduces the silver salt, Ag being precipitated, it is necessary to convert it, if it is present, into the *ferric state;* the solution must, therefore, be rendered slightly acid, if it is not so already, with HNO_3; it must then be treated with an excess of H_2S, if any of the members of the 1st group of acids are present, and filtered if necessary; the solution must be gently boiled to expel the H_2S and CO_2, and to convert the ferrous salt into the ferric state; NH_4HO must then be added to the solution slightly in excess, and the solution again boiled until it is *neutral* to test-paper; if a precipitate has been formed, filter and add a solution of $AgNO_3$ to the clear liquid. If the solution becomes acid after the addition of the silver solution, it ought to be *very carefully* neutralized with NH_4HO; if no precipitate is produced by $AgNO_3$, *all the acids* of the group, with the exception of those got rid of, are *absent.* If a precipitate is produced, its colour ought to be observed; HNO_3, entirely free from HCl, must be added, and the mixture shaken; if the whole of the precipitate, or a portion of it is dissolved one or more of the acids whose silver salts are soluble in HNO_3 are present; if the whole or a portion of the silver precipitate is insoluble in HNO_3, HCl, HBr, HI, HCN, or their radicals, may be present. As $AgNO_3$ causes no precipitate in solutions of mercuric cyanide, if Hg in the mercuric state is present, cyanogen may be present, although $AgNO_3$ produces no precipitate; cyanogen must, therefore, be examined for according to par. 502, when mercury is present.

When the silver precipitate does not entirely redissolve in HNO_3, examine the original solution for Cy, I, Br, and Cl.

FOURTH GROUP.

527. Acids which are not precipitated by any reagent—NITRIC and CHLORIC ACIDS. A special examination must always be made for the acids contained in this group.

528. We will now give directions for testing for each acid individually by means of characteristic tests, and afterwards the methods to be pursued in preparing solutions for the examination of the acids.

CHARACTERISTIC TESTS FOR THE INORGANIC ACIDS.

529. The characteristic tests must be applied to the original solution; a separate portion must be taken for each acid.

530. ARSENIOUS ACID, ARSENIC ACID, CHROMIC ACID.—As these acids are discovered in testing for the bases, no experiments require to be made for their detection when testing for the acids.

531. SULPHURIC ACID.—The presence or absence of this acid is ascertained on testing a part of the solution with the general reagent, $BaCl_2$, and if a precipitate is produced digesting it in dilute HCl or HNO_3, if it dissolves the acid is absent, if it does not dissolve it is present (404).

532. BORACIC ACID.—This acid can be detected in most cases, by the method described in par. 419; but the most certain test is the one described in par. 420.

533. PHOSPHORIC ACID.—When the phosphates are soluble in ammonic solutions (and the student can decide this when he knows what bases are present), this acid can be detected by the method described in par. 424, but the most certain tests are 427 and 428, especially the last. The student must, however, remember that arsenic acid gives precipitates with these reagents, similar to those given by phosphoric acid; when present, it must, on this account, be removed from the

solution by H_2S, or be reduced to the state of arsenious acid, before testing for phosphoric acid. PO_4 may also be detected by the method given in par. 431.

534. CARBONIC ACID.—This acid is distinguished from the other gaseous acids by giving a precipitate with lime-water; the way for evolving the gas, when combined, and testing it, when liberated, with lime-water, is described in pars. 441 and 442.

535. OXALIC ACID.—This acid is detected by the method described at 449; but very minute quantities of it are more securely detected by boiling the substance with a solution of Na_2CO_3, for some time; subsequently filtering, and acidifying the filtrate with acetic acid, and then adding to it a solution of $CaSO_4$ (451).

536. SILICIC ACID.—To test for this acid, evaporate the solution to dryness with an acid, and proceed as directed at 453 or 455.

537. HYDROFLUORIC ACID.—Test for this acid, when silicic acid is absent, by the method described at 460; when silicic acid is present, by the one described at 462 or 463.

538. SULPHIDE OF HYDROGEN.—This acid is distinguished from the other gaseous acids by giving, with soluble salts of silver and lead, black precipitates; the way for applying the test is described in par. 468. The sulphur in sulphides which are not decomposed by HCl, but require for their decomposition HNO_3, or aqua regia, cannot be detected in this way: recourse must be had in these cases to the process described in par. 471.

539. HYDROCHLORIC ACID.—When HBr and HCy are absent, the presence of this acid is proved by the insolubility of the silver precipitate in HNO_3, and by its solubility in NH_4HO; when HCy is present, and HBr absent, its presence is proved, if, after igniting the silver precipitate, which was insoluble in HNO_3 but soluble in NH_4HO, a whitish residue remains, which is insoluble in HNO_3. When HBr is present, no matter whether HCy is present or absent, the presence of HCl can only be ascertained by the test described at 474.

540. Hydriodic Acid.—Iodine is best discovered by the test described at 486.

541. Hydrobromic Acid.—Examine for Br, according to the method given in par. 494; in the presence of I or Cl, according to par. 495.

542. Hydrocyanic Acid.—This acid can be distinguished from all other acids by the tests described in pars. 499, 501, and 503; if, however mercuric compounds are present which will have been discovered in testing for the bases, the process described in par. 502 must be employed.

543. Nitric Acid.—The tests described at 507, 508, 512, 513, or 514, may be employed, but for the detection of the acid in waters the tests described at pars. 509 and 510 are the best.

544. Chloric Acid.—The presence or absence of this acid is proved by the tests described at 521 and 522.

545. *Preparation of the solutions and examination for the acids.*

The examination for the metallic or basic constituents must always precede the examination for the acids, for in the search for acids, the student will be greatly assisted by knowing what basic substances are present, which of their salts are soluble in water and the reaction of the aqueous solutions of those salts on vegetable colours, also which of the salts of the metals found are insoluble in water, but soluble in acids, and which of them are insoluble both in water and acids. He will, from a knowledge of the metals present, the solubility or insolubility of the substance under examination in water or acids, be able to form a tolerably correct conclusion as to the acid or acids which must be absent; thus, for instance, if the substance is a solid soluble in water, or it is a solution, water being the solvent, and the solution in either case is ***neutral*** to test-paper and the basic constituents present are K, Na and NH_4, all the acid radicals whose salts of K, Na and NH_4, are alkaline to test-paper must be absent, and if any polybasic acid radical is present which class of salts of this radical it is that is present will also be known. To take another example: if Ba, K and Na, were the metals present and the solution was neutral to test-paper all the acid radicals whose baric salts are *insoluble* in water, and all the soluble salts of Ba, K, and Na that are *alkaline* or *acid* to test-paper, must be absent. Again SO_4 or Cl need not be sought for in soluble compounds containing Ba or Ag respectively.

546. If the substance is a solid soluble in water, or it is a solution, water being the solvent, and if any of the members of the 1st group of acids or CO_2, or H_2S, have been detected, they must be got rid of and the solution neutralized as described at par. 525-*a*, the solution must then be examined for the other acids, as there directed. If none of the acids of the first group, nor CO_2, or H_2S, have been detected, proceed at once with the examination for the other acids according to par. 525-*a*, if the solution is *neutral;* if it is *alkaline*, first render it exactly neutral with HNO_3, and then proceed with the examination: if it is *acid*, neutralize it with NH_4HO; filter, if necessary, and then proceed with the examination according to 525-*a*.

547. If the substance is insoluble in water but soluble in acids, or if it is a solution an acid being the solvent, it is better in the majority of cases to get rid of all the metals but the alkaline ones, as the presence of some of the other metals interferes with the detection of some of the acids; they may be got rid of by one or other of the three following methods.—1. Precipitate the members of the 5th and 6th group of bases, when they are present, from the acid solution with H_2S; filter, boil the filtrate gently until the excess of H_2S, is expelled, then add a solution of Na_2CO_3 (entirely free from sulphate and chloride), in excess, and then a little Na_2CO_3, in the solid state, and boil for some time; 2nd. Boil the *dry solid* with an excess of a concentrated solution of Na_2CO_3, for some time; 3rd. Mix the solid with four parts of $NaKCO_3$, and fuse the mixture; boil the fused mass in water; whichever of these plans has been adopted the bases remain in the residue, and the acid radicals in combination with the Na; filter and add to the filtrate HNO_3, slightly in excess, heat the solution gently, taking care that it remains permanently acid, until all the CO_2 is expelled, then add NH_4HO, slightly in excess, again warm the solution until it is

neutral to test-paper; if a precipitate has been formed, filter and examine the clear solution according to par. 550.

548. It is not necessary to remove the bases in order to test for H_2SO_4, HCl, and HNO_3. All the chlorates are soluble in water, and so are all the nitrates, with the exception of a few basic ones; if a substance is, therefore, entirely insoluble in water, chlorates must be, and nitrates probably are, *absent;* if a portion only of a substance is soluble in water, treat a portion of the substance with water, and examine the aqueous solution *specially* for the acids of the fourth group.

549. In testing for the acids the general reagents are used in most cases only to prove the presence or absence of an entire group of acids. The detection of each of the acids in the groups requires the further application of the characteristic tests, par. 529.

550. Test a portion of the solution with one of $BaCl_2$ or $Ba(NO_3)_2$, as directed at par. 525; test another portion with one of $AgNO_3$, as directed at par. 526, then test specially for the acids indicated by these reagents, and also for those of the fourth group.

551. *Preliminary examination for acids.*—By heating the substance with concentrated H_2SO_4 the presence or absence of *volatile inorganic acids* is at once ascertained, these acids either volatilizing undecomposed, or yielding volatile products of decomposition. For this purpose a small portion of the dry substance is heated in a test-tube (not to boiling), with three or four times its volume of concentrated H_2SO_4; when, in the case of all acids which are either volatile without decomposition, or are decomposed by H_2SO_4 at a high temperature, gases or vapours are evolved, the properties of which, in most cases, indicate the nature of the acids present. The following table exhibits the behaviour of the salts of the volatile acids with concentrated H_2SO_4:—

WITHOUT DECOMPOSITION.	WITH DECOMPOSITION.
CO_2. Inodorous; causes a *precipitate* in lime-water.	HI. Violet vapours of I, which colour starch-paste *blue*.
SO_2. Odour of burning S; turns a solution of K_2CrO_3 *green*.	HBr. Red vapours of Br, which colour starch-paste *orange*.
H_2S. Odour of rotten eggs; turns paper moistened with a lead solution *brown*.	HCN. Disengages CO, which burns with a *blue flame*.
HCl. Irritating gas, which gives white fumes in contact with NH_3.	CrO_3. Evolves O, the solution becoming *brown* or *green*.
HF. Fuming gas, which corrodes glass.	$HClO_3$. *Greenish yellow* explosive gas.
HNO_3. Colourless acid gas, sometimes having brownish tint from a portion of it being decomposed; on the addition of copper filings *red fumes*, which colour starch paste and KI *blue*.	$H_2C_2O_4$. Evolves CO_2 and CO.

552. It must be observed that the behaviour of a mixture of salts when heated with H_2SO_4 is often different to the behaviour of the salts when heated separately with H_2SO_4; thus, for instance, a mixture of a nitrate and chloride, when heated with H_2SO_4, evolves Cl, and red nitrous fumes. Mercury and tin chlorides are decomposed with difficulty, if at all, by H_2SO_4.

553. Answers to the following exercises must be written out.

EXERCISES.

143. Describe the chemical reactions involved in the etching of glass.

144. How can small quantities of $HClO_3$ be recognised in the presence of HCl?

145. What is meant by stating that a water is hard? and describe Clarke's process for softening hard water.

146. What is the action of H_2S and SO_2 on highly oxidised bodies? Illustrate your answer by diagrams showing the action of H_2S on Fe_23SO_4 and SO_2 on $K_2Cr_2O_7$.

147. What changes do NiC_2O_4 and CoC_2O_4 undergo when heated in close vessels?

148. What is the action of HCl and H_2SO_4 on chromates? Illustrate your answer by diagrams.

149. How is iodine prepared on the manufacturing scale?

150. How is fluorine detected in the presence of silicates?

151. Describe the properties and some of the transformations of $H_2C_2O_4$.

152. How is HCy prepared? what transformations does it undergo in the presence of acids and alkalies? and give the different methods for ascertaining its presence.

153. What change do the neutral and acid chromates of the alkaline metals undergo on being heated?

154. What is the action of HF upon SiO_2 in the presence of water?

155. Chrome iron ore in fine powder is mixed with chalk, and the mixture is heated to bright redness in a current of air in a reverberatory furnace for nine or ten hours, the mixture being frequently stirred; it is afterwards treated with water, the clear solution drawn off from the insoluble matter, and H_2SO_4 is then added to the solution until it is slightly acid; K_2CO_3 is then added, the mixture is afterwards filtered, and the solution is evaporated until crystals begin to form. What change does the chrome iron undergo in roasting? what is dissolved out of the roasted mass by the water? why is the H_2SO_4 added? what change does the K_2CO_3 effect? and, finally, what substance is it that crystallizes out?

156. What takes place when a mixture of NaCl, K_2CrO_4, H_2SO_4 is submitted to distillation?

157. Acids which form insoluble lead salts are frequently separated from other acids and substances which are not precipitated by lead salts, by means of lead acetate or nitrate, and washing the precipitate to free it from the other impurities and the excess of the soluble lead salt added, afterwards sus-

pending the insoluble lead salt in water, and passing H_2S through the mixture to excess; the lead is converted into insoluble PbS, whilst the acid remains in solution; could chromic acid be purified in this manner? Give reasons for the opinion expressed.

158. Describe the effect of heat on the following phosphates, Na_3PO_4, Na_2HPO_4, and NaH_2PO_4.

159. Is there any method of disintegrating a silicate insoluble in acids without fusing it?

ORGANIC ACIDS.

554. Organic acids cannot be detected with the same certainty and precision as the inorganic acids. To detect with certainty even some of those which we have given requires on the part of the analyst great skill and judgment. The special properties of each of the acids are first described, their division into groups, with a description of the properties of each group of acids, and afterwards the processes to be followed in preparing solutions for their examination.

BEHAVIOUR OF THE ACIDS AND THEIR RADICALS WITH REAGENTS.

TARTARIC ACID, $H_2H_2C_4H_2O_6 = H_2\overline{T}$.

SOLUTION FOR THE REACTIONS, $NaHH_2C_4H_2O_6$ *in water.*

555. This acid is tetratomic, but only *two of its four replaceable atoms of H can be replaced by metals*, the other two are replaceable by alcoholic and acid radicals. This acid forms with monatomic metals both acid and neutral salts, for example, hydric potassic tartrate $KHH_2C_4H_2O_6$, potassic tartrate $K_2H_2C_4H_2O_6$, potassic sodic tartrate (Rochelle salt) $KNaH_2C_4H_2O_6$; with diatomic metals it forms neutral salts, having the general formula $M''H_2C_4H_2O_6$; one of the commonest tartrates is the so called tartar emetic $KSbOH_2C_4H_2O_6$, which may be considered as containing the monatomic radical SbO in place of an atom of H, or a monatomic metal.

556. This acid exists in grapes, tamarinds, and many other fruits; it is deposited during the fermentation of the grape juice as the acid potassic salt $KHH_3C_4H_2O_6$, this deposit is called in commerce crude *tartar*, or *argol*, and when purified by recrystallization, *cream of tartar*. The acid is obtained by precipitating from the tartar solution the calcic salt, and decomposing this salt with dilute H_2SO_4, and then evaporating the solution to the crystallizing point. It occurs in the form of colourless, transparent crystals; it dissolves in cold, as well as in hot, water, and is soluble also in alcohol, the solution is acid to test-paper, and if kept for a short time, becomes mouldy and decomposes. It can be produced artificially by acting upon milk sugar with HNO_3; it is also obtained by treating dibromosuccinic acid, $C_4H_4Br_2O_4$, with Ag_2O, in the presence of water, thus :—$C_4H_4Br_2O_4 + Ag_2O + H_2O = C_4H_6O_6 + 2AgBr$.

By the action of HI or iodide of phosphorus, it is reduced to malic, or to succinic acid:

$$(1)\quad C_4H_6O_6 + 2HI = \underset{\text{Malic acid.}}{C_4H_6O_5} + I_2 + H_2O,$$

$$(2)\quad C_4H_6O_6 + 4HI = \underset{\text{Succinic acid.}}{C_4H_6O_4} + 2I_2 + 2H_2O,$$

In the presence of oxidizing agents it is converted (generally) into carbonic, formic, and oxalic acids. When fused with KHO the acid and tartrates break up into an acetate and an oxalate:—$C_4H_6O_6 + 3KHO = KC_2H_3O_2 + K_2C_2O_4 + 3H_2O$.

557. The acid and its salts, when heated, char, and emit a peculiar and very characteristic odour, resembling that of burnt sugar, which is best perceived when the substance is heated in a tube open at both ends. If the acid, or a tartrate in the solid state, be heated with concentrated H_2SO_4, the mixture acquires a black or a brownish-black colour, owing to the separation of carbon, which takes place simultaneously with the evolution of CO. If a solution of potassic perman-

gate be rendered strongly alkaline, and a tartrate be added and the solution boiled, the solution becomes decolorised, the permangate being reduced to MnO_2.

558. The tartrates of the alkaline metals, and of those of the 3rd and 4th groups are soluble in water. The tartrates that are insoluble in water are soluble in HCl or HNO_3.

559. As tartaric acid is a test for K, so in like manner potassic salts, especially the acetate, can be employed as a test for tartaric acid, free and combined; for this purpose a concentrated solution of potassic acetate is added to the solution, and the mixture is then shaken very violently, as the precipitate is greatly promoted by shaking, and the addition of an equal volume of alcohol heightens the delicacy of the reaction.

560. $BaCl_2$ produces in solutions of the tartrates a white precipitate of $BaH_2C_4H_2O_6$, which is soluble in solutions containing ammonic salts and in HCl.

561. $CaCl_2$ precipitates from solutions of the tartrates a white precipitate of $CaH_2C_4H_2O_6$, $4H_2O$, which is soluble in acetic and the mineral acids; ammonic salts retard the formation of the precipitate. It is distinguished from calcic phosphate, calcic borate, and calcic oxalate, by dissolving in a cold not over-dilute solution of KHO, from which solution it is precipitated on boiling, and again redissolved as the liquid cools.

562. *Lime-water* produces in solutions of the tartrates and also in solutions of the acid, if added until the solution is alkaline, a white flocculent precipitate of calcic tartrate, which becomes crystalline after some time; this precipitate is soluble in tartaric acid and in solution of NH_4Cl, from which solutions the calcic tartrate separates after some time in the crystalline form.

563. Plumbic acetate produces in solutions of tartaric acid and the tartrates a white precipitate of $PbH_2C_4H_2O_6$, which dissolves readily in HNO_3, in NH_4HO, in tartaric acid, and in ammonic tartrate.

564. $AgNO_3$ produces, in solutions of the *neutral* tartrates, a white precipitate of $Ag_2H_2C_4H_2O_6$, which is soluble in

NH_4HO; if the ammonic solution be gently heated a bright metallic deposit of silver is formed.

CITRIC ACID, $H_3HC_6H_4O_7$.

Solution for the reactions $Na_3HC_6H_4O_7$ *in water.*

565. This acid is tetratomic, but only three of its four replaceable atoms of H can be replaced by metals; the fourth is called alcoholic hydrogen. It forms with the alkali metals, one neutral and two acid salts, *ex.* tripotassic citrate $K_3HC_6H_4O_7$, hydric dipotassic citrate $K_2HHC_6H_4O_7$, and dihydric potassic citrate $KH_2HC_6H_4O_7$; it forms with dyad metals two classes of salts having the following general formulæ: $M''HHC_6H_4O_7$ and $M''_3(HC_6H_4O_7)_2$.

566. This acid exists in lemons, oranges, citrons, gooseberries and many other fruits; it is prepared from lemon-juice by neutralizing it with chalk, after it has fermented a little to separate the mucilage and other impurities; the lime salt thus obtained is decomposed with dilute H_2SO_4, and the solution evaporated to the crystallizing point. It forms large transparent crystals, it is very soluble in hot and cold water, and also in alcohol; its solution is acid to test-paper, and decomposes on keeping. Fused with KHO it gives potassic acetate and oxalate — $C_6H_8O_7 + 4KHO = 2KC_2H_3O_2 + K_2C_2O_4 + 3H_2O$.

567. Citric acid chars when heated; the charring is attended with an evolution of pungent fumes which cannot be mistaken for those evolved by tartaric acid. If the acid or a citrate in the solid state be heated with concentrated H_2SO_4, CO, and CO_2 are evolved without any change of colour in the liquid; the mixture blackens only after long boiling. If a solution of potassic permanganate be rendered strongly alkaline, and a salt of citric acid be added and the mixture boiled, the solution gradually becomes green, and so remains on continued boiling.

568. Both the neutral and acid salts of the alkaline citrates are readily soluble in water; citric acid is not, therefore, precipitated from its solutions on the addition of potassic acetate.

Citric acid, like tartaric acid, prevents the precipitation of alumina, ferric oxide, and other bases, by the alkalies.

569. A solution of $BaCl_2$ produces in solutions of the citrates a white precipitate of baric citrate, which is soluble in much water, in free acids, and in solutions of ammonic salts.

570. A solution of $CaCl_2$ produces in solutions of citrates, but not in citric acid, a precipitate of calcic citrate, which is more insoluble in hot water than cold, insoluble in KHO, soluble in a cold solution of NH_4Cl, from which it is precipitated on boiling the solution. Free citric acid must be neutralized by KHO or NaHO before adding $CaCl_2$ to its solution.

571. Lime-water produces no precipitate in cold solutions of citric acids or the citrates; but on boiling the solution a precipitate is produced, which redissolves almost entirely when the liquid becomes cold.

572. If a solution of ferric tartrate is evaporated on the water-bath to a syrupy consistence, a solid basic salt is deposited, but ferric citrate under the same circumstances deposits no solid salt. Upon this difference of deportment of the ferric salts of the two acids has been based a method for the detection of tartaric acid in citric acid; by this method even minute quantities of tartaric acid admit of being detected in citric acid; the following is the method:—the citric acid to be examined is dissolved in water, hydrate of ferric oxide is added to the solution in excess and the mixture is heated to about 90° C. When the acid has become saturated with oxide the iron is filtered off from the undissolved portion; the solution is then evaporated on the water-bath to a syrupy consistence; if the citric acid contained tartaric acid, there would be formed a deposit of an insoluble basic ferric tartrate; if, on the contrary, the citric acid is pure, there is no deposit from the syrupy liquid, it remains perfectly clear.

573. A solution of plumbic acetate, when added in excess, produces in solution of citric acid a white precipitate of $PbHHC_6H_4O_7,H_2O$, which, when washed, dissolves readily in ammonia.

574. Tartaric and citric acids are largely used by calico

printers as discharges in the production of white spots on a coloured ground.

MALIC ACID, $H_2C_4H_4O_5$.

Solution for the reactions, $Na_2C_4H_4O_5$.

575. This acid contains only two atoms of H replaceable by metals, although it is, probably, a triatomic acid. It forms with the alkaline metals a neutral and an acid salt; it forms, also, with calcium and other diatomic metals, an acid as well as a neutral salt. Nearly all the malates are soluble in water. It is the acid of apples, pears, and various other fruits. It crystallizes with great difficulty, it is deliquescent, and is soluble in alcohol as well as water; its solution is acid to test-paper, and becomes mouldy and decomposes by keeping. It can be produced artificially by the action of moist Ag_2O on monobromosuccinic acid.

$$2C_4H_5BrO_4 + Ag_2O + H_2O = 2C_4H_6O_5 + 2AgBr.$$

It is also produced by the action of nitrous acid on asparagin, and on aspartic acid.

$$(1)\ \underset{\text{Asparagin.}}{C_4H_8N_2O_3} + 2HNO_2 = C_4H_6O_5 + 2H_2O + 2N_2.$$

$$(2)\ \underset{\text{Aspartic acid.}}{C_4H_7NO_4} + HNO_2 = C_4H_6O_5 + H_2O + N_2.$$

By the action of HI it is converted into succinic acid—$C_4H_6O_5 + 2HI = C_4H_6O_4 + H_2O + I_2$. If kept at a temperature of 150° C., it is slowly resolved into water and fumaric acid ($C_4H_4O_4$); if kept for some hours between 175° and 180°, it is resolved into water, fumaric acid, and maleic acid, an acid isomeric with fumaric acid. Fused with KHO it splits up like tartaric and citric acids into oxalic and acetic acids. Concentrated H_2SO_4 decomposes the acid and the malates in the solid state with evolution of CO; the mixture blackens only after long boiling.

576. A solution of $CaCl_2$ does not produce a precipitate in solutions of the free acid or its salts until alcohol is added.

577. "Lime-water produces no precipitate in solutions of free malic acid, nor in solutions of malates. The fluid remains perfectly clear even upon boiling, provided the lime-water is prepared with boiling water."

578. A solution of lead acetate throws down, from a solution of the acid or its salts, a white precipitate of $PbC_4H_4O_5, 3H_2O$. If the fluid in which the precipitate is suspended is boiled, the precipitate fuses to a mass resembling resin melted under water. But this reaction is only distinctly marked when the plumbic malate is tolerably pure; if mixed with other lead salts, it does not present this appearance, or at least imperfectly.

BENZOIC ACID, HC_7H_5O.

Solution for the reactions, $NH_4C_7H_5O$, *in water.*

579. This acid is monatomic. It is contained in gum benzoin. The pure acid appears under the form of white scales or needles, or simply as a crystalline powder. It is readily dissolved by alcohol and ether; it is only slightly soluble in cold water; on the addition of HCl to an aqueous solution of any of its salts, it separates from the solution as a white crystalline powder. It volatilizes completely when heated, with partial decomposition, the fumes cause a peculiar irritating sensation, and provoke coughing. When heated in a tube open at both ends, a portion of the acid condenses upon the cool part of the tube. When heated with concentrated H_2SO_4 it volatilizes without carbonizing.

580. It can be produced artificially by oxidizing bitter almond oil, or by boiling hippuric acid with HCl, or by oxidizing benzilic alcohol.

581. $BaCl_2$ and $CaCl_2$ do not precipitate this acid under any circumstances.

582. Fe_2Cl_6 produces in neutral solutions of this acid a precipitate of ferric benzoate, the colour of which is pale buff;

NH_4HO in excess withdraws the acid from this precipitate, $Fe_2H_6O_6$ remaining. Ferric benzoate differs from ferric succinate in this—that it dissolves in a little HCl with separation of the greater portion of the benzoic acid.

SUCCINIC ACID, $H_2C_4H_4O_4$.

Solution for the reactions, $(NH_4)_2C_4H_4O_4$, *in water.*

583. This acid is bibasic, it therefore forms an acid and a neutral salt with the alkaline metals. It occurs ready formed in amber and in certain lignites. It is crystalline and melts at 180°, but begins to emit suffocating vapours below its melting point; it does not carbonize when heated. It is more soluble in hot than cold water; it is less soluble in alcohol, and nearly insoluble in ether. Fused with KHO it yields a carbonate and an oxalate, together with a gaseous hydrocarbon. It offers great resistance to the action of oxidizing agents; in fact it is a frequent product of the oxidation of organic substances, especially fats. It is also formed in many processes of fermentation, and we have already noticed that it is produced from malic and tartaric acids, by acting on them with HI. It is not attacked by concentrated H_2SO_4, even when heated.

584. The succinates of the alkali-metals and of magnesium are easily soluble in water; those of the alkaline earth metals, and most other diatomic metals, are sparingly soluble; those of the sesqui-atomic metals are insoluble.

585. $BaCl_2$, after the addition of NH_4HO and alcohol, precipitates this acid from its solutions in the form of $BaC_4H_4O_4$, benzoic acid does not exhibit this reaction; succinic acid is further distinguished from benzoic acid by not being precipitated from its soluble salts by the mineral acids.

586. Fe_2Cl_6 produces, in neutral solutions of the succinates, a precipitate of the ferric succinate, the colour of which is reddish-brown. It is decomposed in the same manner as ferric benzoate by NH_4HO.

TANNIC ACID (Tannin) $H_3C_{27}H_{19}O_{17}$.

Solution for the reactions, the acid in water.

587. This acid is a solid body, of a light straw colour, and not crystalline. It is very soluble in water; the solution absorbs oxygen from the air, which converts the acid into two others, gallic and ellagic. It is precipitated from concentrated solutions by dilute H_2SO_4 and HCl, in the form of a paste. It is also precipitated by dilute starch-paste, by gelatine, and albumen. It is completely removed from its solutions by placing in the liquid a piece of animal membrane.

588. Fe_2Cl_6 produces, in solutions of tannic acid or tannates, a dark blackish-blue precipitate.

589. Tartar emetic gives in solutions of this acid a white gelatinous precipitate.

590. Concentrated H_2SO_4, treated with the acid or the tannates in the solid state, produces a dark purplish-black liquid immediately, but does not evolve CO.

GALLIC ACID, $H_3C_7H_3O_5$.

Solution for the reactions, the acid in water.

591. This acid is tribasic, it therefore forms with the monatomic metals three series of salts. It is contained in green and black tea, and in many other plants. It can be produced artificially by the action of acids or alkalies on tannic acid. It crystallizes in prisms of a silky lustre, of a very pale-yellow colour. It is not very soluble in cold water, but dissolves in three parts of boiling water. Its alkaline solutions, when exposed to the air, become first yellow, then green, red, brown, and finally nearly black, owing to the absorption of oxygen. It is not precipitated by gelatine or animal membrane. By this behaviour it may be distinguished and separated from tannic acid.

592. Fe_2Cl_6 produces, in solutions of this acid and its salts, a bluish-black colour.

593. Concentrated H_2SO_4 behaves with gallic acid much in the same way as with tannic acid.

ACETIC ACID, $HC_2H_3O_2$.

Solution for the reactions, $NaC_2H_3O_2$, *in water*.

594. This acid, so well known under the name of vinegar, is monobasic; the normal salts are all soluble in water; the normal acetates of the alkali metals can combine with a molecule of acid as they do with water. These salts are called diacetates. Some normal salts in the same way can combine with a molecule of a metallic oxide or its hydrate, and form basic salts. Solutions of ferric and aluminic acetates are decomposed by boiling into basic salts and free acid which is expelled; these salts experience the same decomposition; if a cotton cloth is immersed in their solutions and hung up in a moist and warm atmosphere; this process is called *ageing* by the cotton-printers, and the deposit of the basic salts in the cloth is called a mordant, the commercial names of ferric and aluminic acetate solutions are *iron liquor* and *red liquor*.

595. Acetic acid exists in the juices of many plants, especially of trees. It is formed in the destructive distillation of organic substances, especially of wood. The greater part of the acid used in the arts is obtained from this source, and goes under the name of *wood vinegar*, or pyroligneous acid. Alcohol is converted into acetic acid by various processes of oxidation; in the ordinary processes for making vinegar, either from wine or malt, an alcoholic solution is exposed to the joint influence of air and a ferment. Acetates are formed by heating cyanide of methyl (CH_3CN) with the caustic alkalies, and by acting on sodium-methyl (CH_3Na) with CO_2, and by other processes.

596. It is a colourless crystalline solid below 16° C., above that temperature it is a thin colourless liquid of an exceedingly pungent and well-known odour of vinegar. It is miscible in all proportions with water, alcohol, and ether, and dissolves camphor and several resins. In the liquid state it has a den-

sity of 1·063, and boils at 120° C., its vapour is inflammable On account of its solidifying below 16°, it has received the name of *glacial acetic acid*, in contra-distinction to the mixtures of water and the acid which do not crystallize; it is to these mixtures that the name acetic acid is commonly applied.

597. If Fe_2Cl_6 is added to acetic acid, and the acid is then nearly saturated with NH_4HO, or if a neutral acetate is mixed with Fe_2Cl_6, the fluid acquires a deep dark-red colour, owing to the formation of ferric acetate. By boiling, the fluid becomes colourless if it contains an excess of acetate, the whole of the Fe precipitating as a basic acetate, in the form of brown-yellow flakes. NH_4HO precipitates from it the whole of the Fe as $Fe_2H_6O_6$. By addition of HCl a fluid which is red from the presence of ferric acetate turns yellow (difference from ferric sulphocyanide).

598. Acetic acid or acetates when heated with $HgCl_2$ produce no precipitate of HgCl.

599. When H_2SO_4 is added to acetates, the acetic acid is liberated, and is recognised by its odour of vinegar. If the acetate is distilled with the H_2SO_4, the acetic acid is obtained in the distillate.

600. When acetates are heated with about equal volumes of concentrated H_2SO_4 and alcohol, acetic ether $(C_2H_5,C_2H_3O_2)$ is formed, which is readily distinguished by its characteristic odour.

601. Concentrated H_2SO_4 occasions no blackening when heated with acetic acid or its salts.

602. If an excess of PbO be digested in acetic acid, there is formed a soluble basic lead acetate, which has an alkaline reaction.

FORMIC ACID, $HCHO_2$.

Solution for the reactions $NaCHO_2$ *in water*.

603. This acid is monobasic; all its salts are soluble in water; it occurs in ants, in caterpillars, and in several secretions of the human body; it is present in the juice of the

stinging-nettle and other vegetables; it has been found in some mineral waters. It may be prepared by passing CO over moist KHO; and by passing CO_2 and aqueous vapour over K at a moderate heat, $KHCO_3$ being formed at the same time; it is also formed by acting on HCN with an alcoholic solution of KHO; and by distilling dry oxalic acid mixed with glycerin, which takes no part in the decomposition, but appears to act by preventing the temperature rising too high; it is formed by the partial oxidation of a great variety of organic bodies, as starch, gum, tartaric acid, &c.

604. This acid is a clear colourless liquid which fumes slightly in the air; it has an exceedingly penetrating odour; it boils at 101·1° C., and crystallizes in large brilliant plates when cooled below —1° C. Its sp. gr. is 1·235, and it mixes with water and alcohol in all proportions. When exposed to the action of heat, it volatilizes completely; the vapour is inflammable and burns with a blue flame.

605. The formates are all decomposed by heat; the formates of the alkalies and alkaline earth metals ignited out of contact with air leave carbonates slightly blackened by charcoal, CO and H being evolved;* the formates of other metals (copper and lead for example) when heated give off CO, CO_2, and H_2O, the metal being left in the metallic state. NH_4CHO_2 when exposed to a high temperature is decomposed into HCN and H_2O.

606. If Fe_2Cl_6 is added to a neutral formate, the fluid acquires a blood-red colour; the liquid becomes colourless on boiling if an excess of the formate be present, all the iron being precipitated in the form of a basic salt. The formates, in fact, exactly resemble the acetates in their behaviour with ferric salts.

607. This acid is a powerful reducing agent; it reduces the oxides of the *noble metals*, yielding H_2O and CO_2; by heating it with a solution of $AgNO_3$ the Ag is deposited sometimes in the pulverulent state and sometimes as a specular coating

---

* Baric formate yields the products above mentioned, together with gaseous hydrocarbons, viz. marsh-gas, ethylene, and tritylene.

on the glass tube; this reaction distinguishes it from acetic acid, which does not reduce the silver nitrate.

608. If the acid or an alkaline formate is heated to from 60° to 70° C. with $HgCl_2$, $HgCl$ precipitates. If the mixture is heated to 100° C., Hg separates along with $HgCl$.

609. When dilute H_2SO_4 is added to formates the acid is liberated and is recognisable by its odour; if the formiate is distilled with the H_2SO_4, the formic acid is obtained in the distillate.

610. Upon heating a formate with a mixture of H_2SO_4 and alcohol, formic ether ($C_2H_5CHO_2$) is produced, which has an agreeable odour resembling peach kernels.

611. Concentrated H_2SO_4, when heated with formic acid or a formate, decomposes the acid into CO and H_2O; there is therefore no blackening, however long the heat may be continued.

URIC ACID, $H_2C_5N_4H_2O_3$.

Solution for the reactions, the acid.

612 This acid is bibasic; it therefore forms two series of salts with the monatomic metals, viz. neutral salts and acid salts. "It is a product of the incomplete oxidation of animal tissues. In combination chiefly with ammonia it forms the principal urinary constituent voided by insects, land-reptiles, and birds (whence it is found in guano). Normally it occurs but in small proportion in the urine of man, and is found in yet smaller proportions in that of carnivorous quadrupeds, and can scarcely be said to exist in that of herbivorous and omnivorous quadrupeds." The solid white excrement of serpents consists almost entirely of uric acid and ammonic urate. This acid has never yet been formed by artificial means.

613. This acid occurs in delicate white needles; it is scarcely soluble in cold water, dilute HCl or $HC_2H_3O_2$; it is soluble in alcohol and ether. It dissolves in concentrated H_2SO_4 without apparent decomposition, and is precipitated by dilution with water. It is soluble in the alkalies and alka-

line salts, from which solutions it is precipitated on the addition of acids.

614. Urates, with the exception of the *potassic* and *sodic* ones, are almost all insoluble in water; the ammonic salt is extremely insoluble in water; it is however dissolved by NaCl or Na_2HPO_4, sodic urate being formed.

615. The CALCIC SALT is white; the FERRIC SALT brown; the COPPER SALT green; the SILVER SALT white, rapidly becoming black if the liquid be heated; the MERCURY and LEAD SALTS are white.

616. Uric acid yields by destructive distillation cyanic, hydrocyanic, and carbonic acids, ammonic carbonate, and a black coaly residue rich in nitrogen. By fusion with KHO it furnishes carbonate cyanate and cyanide of the alkaline metal.

617. It dissolves with the aid of heat in dilute HNO_3; the solution is attended with effervescence and evolution of red fumes, the uric acid being oxidized at the expense of the HNO_3. If the HNO_3 solution be evaporated in a porcelain dish on the water bath just to dryness, and a glass stopper moistened with strong ammonia-water be then held over the residue in the dish, a *magnificent purple colour* is produced, owing to the formation of MUREXIDE ($C_8N_6H_8O_6$).

618. If uric acid be dissolved in sodic carbonate, and a drop of the solution be laid on paper moistened with silver solution, a *brown spot* is formed, argentic carbonate being reduced by uric acid at ordinary temperatures.

619. Concentrated H_2SO_4 dissolves uric acid, with the aid of heat, without change; if the heat be long continued, the liquid becomes dark.

CLASSIFICATION OF THE ORGANIC ACIDS, WITH A DESCRIPTION OF THE PROCESSES TO BE FOLLOWED IN THE EXAMINATION OF SUBSTANCES FOR THESE ACIDS.

Classification of the acids.—The organic acids described in this part (Part I) of this book may be conveniently divided into four groups, as follows :—

FIRST GROUP.

620. *1st Division.*—Acid which is precipitated from *neutral* solutions in the cold by $CaCl_2$, TARTARIC ACID ; the properties of calcic tartrate are given in par. 561. *2nd Division.* Acid which is precipitated by $CaCl_2$ from boiling solutions rendered alkaline by lime-water, CITRIC ACID. *3rd Division.*—Acid which is not precipitated from hot or cold solutions by $CaCl_2$, but its calcic salt is precipitated on adding alcohol to the solution, MALIC ACID.

Oxalic, boracic, phosphoric, hydrofluoric, carbonic, arsenious, and arsenic acids are also precipitated from neutral solutions by $CaCl_2$.

SECOND GROUP.

621. *1st Division.*—Acids which give precipitates in *neutral* solutions with Fe_2Cl_6, TANNIC, BENZOIC, and SUCCINIC ACIDS. Tannic acid gives a precipitate with Fe_2Cl_6 in acid, as well as neutral solutions. The iron salt does not precipitate benzoic and succinic acids in the presence of a citrate.

2nd.—Acids which give a coloration in *neutral* solutions with Fe_2Cl_6, ACETIC, FORMIC, and GALLIC ACIDS; the two former give a reddish and the latter a black coloration.

PHOSPHORIC, ARSENIC, and BORACIC ACIDS give precipitates in *neutral* solutions with Fe_2Cl_6, the first two in acid as well as neutral solutions.

THIRD GROUP.

622. Acids which are precipitated from neutral solutions by $AgNO_3$. TARTARIC, CITRIC, MALIC, BENZOIC, SUCCINIC, AND FORMIC ACIDS. Argentic tartarate, and argentic formate are reduced on being heated, Ag separating.

FOURTH GROUP.

Acetic acid, uric acid.

623. These acids are not precipitated by the group reagents, nor do they give any peculiar coloration with them.

DETECTION OF THE ORGANIC ACIDS.

624. TARTARIC ACID.—The peculiar and highly characteristic odour which this acid evolves on ignition (557), prevents it from being overlooked if present in any quantity. But the test with acetate of potash (559) ought to be made in all cases; the solution to be examined for tartaric acid must be neutral, or if acid the free acid must only be acetic acid or tartaric acid. For detecting minute quantities of tartaric acid in the presence of citric acid employ the method described in par. 572.

625. CITRIC ACID.—Oxalic and tartaric acids, if present, require to be removed before examining for this acid, add, therefore, to the solution in *the cold* $CaCl_2$ and lime-water to alkaline reaction; calcic tartrate and oxalate will be precipitated,* filter and heat the filtrate to boiling. Calcic citrate will precipitate; filter and examine the filtrate for malic acid as directed in next par.

626. MALIC ACID.—To the filtrate from the calcic citrate precipitate, is added alcohol, calcic malate will precipitate if that acid be present. Malic acid is further distinguished from tartaric and citric acids, by not being blackened when heated with concentrated H_2SO_4.

627. BENZOIC ACID.—This acid, in the presence of succinic acid, is best detected by treating the iron precipitate of the two acids, after it has been washed, with NH_4HO, and then filtering, and after concentrating the filtrate dividing it into

---

* The separation of calcic tartrate is promoted by agitation. Calcic tartrate is separated from calcic oxalate by treating the precipitate with solution of KHO (561).

two parts, mixing one part with HCl, when benzoic acid. if present, will be precipitated; in the other part, succinic acid is examined for by adding $BaCl_2$ and alcohol (585).

628. SUCCINIC ACID.—This acid is best detected in the presence of benzoic acid, by the method described in the previous paragraph. The student must remember what has been stated in the 2nd group of acids that Fe_2Cl_6 does not precipitate these two acids in the presence of alkaline citrates.

629. TANNIC ACID.—This acid is best detected in the presence of gallic acid, by the method described at 587.

630. GALLIC ACID.—This acid is best detected in the presence of tannic acid, by the method described at 591.

631. ACETIC ACID.—This acid is best detected by the methods described at 597 and 600.

632. FORMIC ACID.—This acid is best detected by the methods described at 607, 608, and 611.

633. URIC ACID.—This acid is best detected by the method described at 617 and 618.

634. PREPARATION OF THE SOLUTION.—When the substance under examination is soluble in water, or if it is in solution and the fluid is water, it requires a little preparation before it can be examined with advantage for the organic acids, as it conduces much to the success of the examination if no other metals but the alkaline ones are present. In order to remove the other metals, the solution has sometimes to be treated with H_2S, and $(NH_4)_2S$; but *generally* it is only necessary to boil the solution with a slight excess of Na_2CO_3; by this reagent the majority of the metals, especially if citric acid is absent, except the alkaline ones, are removed. After the solution has been boiled for some time it is filtered, and to the filtrate is added HNO_3, very slightly in excess; the solution is then gently heated in order to expel the CO_2. After this, NH_4HO is added in very slight excess; and when it is required to have the solution perfectly neutral, as in testing with $AgNO_3$, and Fe_2Cl_6, the solution, which has been rendered slightly alkaline with NH_4HO, is boiled in an evaporating dish until it is neutral to test-paper. When ammonic salts are present in the

substance under examination, the solution must, even if no other metals but the alkaline ones are present, be boiled with Na_2CO_3, until all the NH_4HO is expelled, and the solution is then rendered neutral in the way just stated.

635. When Na_2CO_3 fails to precipitate the metals, as it will frequently when the organic acid is *non-volatile*, especially if it be citric acid, add to the solution neutral lead acetate in excess, collect the precipitate and wash it thoroughly, then suspend it in water and pass H_2S through the mixture to excess, filter off from the PbS, and after expelling the excess of H_2S from the filtrate by heating it, neutralize exactly with Na_2CO_3 and then examine for the acids.

636. It is frequently advisable to separate the volatile acids, for this purpose the solution must be treated, if not acid already, with dilute H_2SO_4, and then distilled in a small retort, the liquid in the retort must be heated gently, not to boiling, and the distillate must be collected; the distillate may contain the following acids:—HCy, HCl, HBr, HI, HNO_3, $HCHO_2$, $HC_2H_3O_2$, $H_2C_4H_4O_4$, and HC_7H_5O.

637. *Preliminary examination for organic acids.* Heat a portion of the dry solid in a test-tube, with 3 or 4 times its volume of concentrated H_2SO_4, the organic acids treated of in this part of the book, show the following behaviour:—Tartaric, tannic, and gallic acids, are immediately blackened; CO_2 is evolved at the same time from tartaric, but not from the other two acids. Citric, malic, and uric acids are not blackened unless boiled with the H_2SO_4, for some time, citric acid evolves CO, and CO_2, and malic acid, CO, on being acted on by H_2SO_4. Benzoic, succinic, and acetic acids are not blackened under any circumstances by H_2SO_4, but they volatilize in an unchanged state. Formic acid is decomposed on being heated with H_2SO_4 into CO, and H_2O without any blackening.

638. Answers to the following exercises must be written out.

EXERCISES.

160. What is the source of tartaric acid, and how is the acid obtained in the free state?

161. How is succinic acid distinguished from benzoic acid?

162. How can formic acid be obtained from inorganic sources, and what is the action of concentrated H_2SO_4 upon it?

163. Give the formula for tartar, Rochelle salt, argol, tartar emetic, and cream of tartar.

164. A crystalline powder, representing a sample of organic acid, is given to you, and you are asked to say whether it is tartaric, citric, or oxalic acid. What tests would you apply for the solution of this problem?

165. How is succinic acid converted into malic and tartaric acids, and how is tartaric acid reconverted into malic and succinic acid?

166. How would you distinguish a tartrate from an oxalate and a citrate respectively?

167. Describe some methods for the manufacture of citric acid, and state some of its applications.

168. Malic acid is extracted from the juice of the mountain-ash berries; there are present along with it small quantities of tartaric and citric acids. The following method is followed for its extraction. Explain the different parts of the process. The juice, after being filtered, is *partly* neutralized with K_2CO_3, but the solution must still redden litmus pretty strongly, solution of Pb $(NO_3)_2$, or $Pb(C_2H_3O_2)_2$, is then added in excess, a curdy precipitate is formed, the mixture is then set aside for some days; with the exception of the mucous flocculent compound of lead and colouring matter, the precipitate by standing becomes converted into small needles; these are carefully freed from the colouring precipitate and other impurities by washing, they are then boiled in a quantity of dilute H_2SO_4 not sufficient to decompose the whole of them, as long as any granular deposit continues to subside: to the mixture is then added an aqueous solution of BaS, until a filtered sample is found to contain Ba;

the liquid is then filtered and the filtrate is boiled with an excess of $BaCO_3$; the mixture is again filtered, and the Ba is precipitated from the filtrate by the careful addition of dilute H_2SO_4; the liquid is again filtered and the filtrate evaporated to the crystallizing point.

169. From the properties and reactions which have been given of oxalic, tartaric, citric, and malic acid, devise another method which, from its cheapness and simplicity, would be suitable as a manufacturing process for the extraction of malic acid from vegetable juice, containing small quantities of oxalic, tartaric, and citric acids.

Examination of Liquids and Solids.

EXAMINATION OF A LIQUID.

639. The student, after he has passed through the different groups of bases and acids, in the manner previously described commences the analysis of liquids, in which he has to look for all these bases and acids, with the exception of the organic acids.*

640. Before commencing the actual analysis, it is necessary to ascertain by preliminary experiments—1. Whether there is *any solid substance* in solution. 2. Whether the solution is *neutral*, *acid*, or *alkaline*.

641. 1st. *To ascertain whether there is any solid substance in solution.*—Evaporate, by a gentle heat, a portion of the liquid

---

* The student will find it conducive to his success in many respects, if he does not engage in the detection of organic acids until he enters upon the examination of solid substances. He will, of course, in *practice*, have always first to ascertain whether organic substances are really present or absent in a solution, before he commences the actual analysis, as the presence of fixed organic matter prevents the detection of many inorganic substances; he will, likewise, in practice, have frequently to separate, by distillation, the liquid from the solid portion of a solution, in order to be perfectly certain that the fluid is *water*, and not any other liquid. This he will ascertain by examining the distilled fluid by the smell, taste, boiling point, specific gravity, &c.

to dryness, on platinum-foil. If no residue remain, it is probably pure water, which will be further confirmed if it has no action upon test-paper. If a residue remain, which is completely volatilized when the temperature is increased, the only basic substances which can be present are NH_4, Hg, As, and Sb. If the residue is not volatile, or at least not completely so, other substances besides these must be present. In both cases it is requisite to perform the next experiment.

642. 2nd. The solution is examined by well-prepared test-papers, as to its neutrality, &c. Each of the three cases which may occur, and the conclusions to which they lead, are considered in pars. 643, 645, 646.

643. The solution is *neutral*. A large number of substances must therefore be absent, because the soluble neutral salts of the greater proportion of the metals possess an acid reaction. The only salts which are neutral to test-papers are the soluble salts of silver and manganese, and some of the soluble salts of the alkalies and alkaline earth metals; some of the salts of these metals are therefore the only ones which can be present; but to distinguish still further, add to a portion of the solution $(NH_4)_2S$, if no precipitate is formed, Ag and Mn are absent, add then to the solution Na_2CO_3 and boil, if this produces no precipitate the metals of the alkaline earths are absent; the only metals therefore which can be present are the alkaline metals. If $(NH_4)_2S$ produces no precipitate, but a precipitate is produced by the Na_2CO_3, the alkaline earths and the alkaline metals have to be sought for, and if both reagents produce a precipitate, the one by $(NH_4)_2S$ being *black*, then all the metals whose salts are *neutral* to test-paper must be sought for. Add HCl in the first instance, filter off from the insoluble AgCl, and add to the filtrate NH_4Cl, NH_4HO, and $(NH_4)_2S$; if a precipitate is produced filter and examine the filtrate for the members of the 2nd and 1st groups in the usual manner.

644. *Examination for the acids.*—Very few acid radicals can be present if Ba, Mn, or Ag are present, as so many of their salts are insoluble in water, and some of the baric salts which are soluble in water are alkaline to test-paper; and if K, Na,

and NH_4 are the only basic radicals that are present, a large number of acid radicals must be absent, as so many of the alkaline salts are alkaline to test-paper; add to separate portions of solution $BaCl_2$ and $AgNO_3$, according to par 550.

645. The solution is *acid*. The acidity may proceed from the presence of a free acid, an acid salt, or a neutral salt having an acid reaction. To ascertain to which of these causes the acidity is due, place the end of a glass rod moistened with a solution of Na_2CO_3, into a portion of the fluid in a watch-glass. If the solution becomes turbid and remains so, it is due to the presence of a neutral salt; if it becomes clear again, the reaction is due either to an acid salt or a free acid. Carbonates and sulphides cannot be present in an acid solution. Examine for the basic constituents in the usual manner. Examine for the acids according to par. 546 if it is a neutral salt having an acid reaction; if an acid salt or a free acid is present, examine according to par. 547.

646. The solution is *alkaline*. The alkalinity may proceed from an alkaline carbonate, silicate, borate, or phosphate; or it may arise from the presence of a free alkali or alkaline earth, or from the cyanogen and sulphur compounds of these metals. If the alkalinity proceeds from ammonia or its carbonate, a large number of substances (those which are insoluble in these reagents) must be absent. If it is due to the presence of the fixed alkalies or their carbonates, a still larger number of substances are excluded. If it is occasioned by the sulphides of the alkaline, or alkaline earth metals, all the metals whose sulphides are insoluble in water and alkaline sulphides must be absent. Examine for the basic constituents in the usual manner, paying strict attention to the precautions given in pars. 376 and 377. Commence the examination of the acids by rendering the solution exactly neutral with HNO_3. If no precipitate is produced on neutralizing the solution, proceed with the examination according to par. 550; if a precipitate is produced on neutralizing the solution, filter, examine the filtrate according to par. 550; and treat the precipitate according to par. 547.

647. The student should never employ the whole of the solution at his disposal, but should always reserve a portion, in the event of any unforeseen accident occurring, and for confirmatory experiments.

648. If the liquid under examination contains inorganic matter in suspension,* the latter, after being separated by filtration, must be brought into solution according to the methods described under the head of "Solid Substances." The solid and liquid portions ought in most cases to be examined separately.

649. Answers to the following exercises must be written out.

EXERCISES.

170. A solid inorganic substance volatilizes completely at a heat below redness. How does this observation simplify its subsequent examination?

171. A solution is neutral to test-paper, and the only metals present are K, Na and Ca, what acids must be absent?

172. A solution is alkaline to test-paper, the alkalinity is due to the presence of ammonic carbonate; what substances must be absent?

173. A solution acid to test-paper is colourless, what substances must be absent?

174. A solution acid to test-paper contains Ba and Ag, what acids must be absent?

EXAMINATION OF SOLIDS.

650. The substance is first examined as to its lustre, colour, odour, and whether it is crystalline or amorphous, since these will frequently afford a means of classifying the substance.

---

* The method of preparing for analysis a solution which is thick or turbid from the presence of organic matter, is described under the head of "Solid Substances containing Organic Matter" (par. 731).

Thus, a metallic lustre will indicate probably a pure metal or an alloy. A blue colour will indicate the probable presence of some salt of copper; a crystalline structure the probable presence of a salt.

651. THE SUBSTANCE WILL EITHER BE A PURE METAL OR AN ALLOY, OR IT WILL NOT.

652. *If it is a pure metal or an alloy* treat it according to par. 737, *after* it has been examined in a glass tube closed at one end and exposed on charcoal to the reducing flame of the blowpipe * (see pars. 656, 2nd and 4th).

653. *If it is neither a pure metal nor an alloy, it will be free from or contain* ORGANIC MATTER which will be ascertained in making the preliminary experiment (par. 656, 2nd). *When it is destitute* of organic matter, treat it according to par. 717. *When it contains* organic matter, according to par. 731.

654. It has already been stated that the substance is submitted to different blowpipe operations before ascertaining in what liquid it will dissolve; the blowpipe operations and the order in which they are to be performed are described in the next paragraph. In these blowpipe experiments, only small quantities of the substance ought to be employed; for if too much is operated upon, uncertain results are the consequence. A particle the size of a mustard seed is sufficient, and that of the flux added about the size of a hemp seed. In reductions, a larger quantity may be employed, because, in that case, the more metal is produced, the more easily can its nature be ascertained. In all cases the substance operated upon must be reduced to the finest powder.

655. We give—1st, *the blowpipe* operations; and 2nd, *Bunsen's flame reactions.*† We recommend the student to make himself acquainted with both modes of examination.

656. The following are the principal blowpipe operations and the order in which they are to be performed:

---

* These are the only blowpipe experiments which require to be made with a pure metal or an alloy.

† The student must study carefully the paragraphs under the head "Blowpipe," in Part III, when he makes these experiments.

1st. Examine whether the substance imparts a colour to the flame, see Table page 244, and par. 660.

2nd. Examine the substance in a glass tube closed at *one* end, see Table VIII, and par. 670.

3rd. Examine the substance in a glass tube *open* at both ends, see par. 676.

4th. Expose the substance to the inner blowpipe flame on charcoal, see Table IX, and par. 682.

5th. Treat the substance with protonitrate of cobalt on charcoal, see Table X, and par. 684.

6th. Examine the substance with carbonate of soda on charcoal, see Table X, and par. 685.

7th. Fuse a portion of the substance with borax on platinum wire, see Table X, and par. 700.

8th. Examine the substance as to its fusibility, see par. 702.

657. COLORATION OF THE FLAME.—As many substances tinge the lamp flame with various characteristic colours, the substance under examination ought to be submitted to the flame in order to ascertain the presence or absence of these substances. To obtain the colour the substance ought to be exposed to the flame on a platinum wire, and the experiment ought to be conducted in a dark room.

658. Merz, who has made a complete investigation of this subject, employs Bunsen's burner, and also a flame of pure hydrogen, and in addition makes use of *blue*, *violet*, *red*, and *green* glasses. The substances which he describes as giving characteristic colours to the flame of Bunsen's burner, in addition to those previously known, are nitric and chromic acids, while phosphoric and sulphuric acids give a peculiar coloration to the dark core of the flame of hydrogen.

659. The flame of Bunsen's burner gives three sorts of colour: *a*. BORDER COLOURS. These are of course peculiar only to the most volatile substances. To produce them, the loop of platinum wire is to be held outside of the flame about one or two millimetres from the lower portion of the outer limit. *b*. MANTLE COLOURS—those, namely, which are seen

when the substance is held in the bright blue-coloured mantle which forms the outer portion of the flame. *c.* **Flame colours.** To produce these, the loop is to be held horizontally and in the hottest part of the mantle. The hydrogen flame yields another species of colour, viz. the **core colours.** These are produced only by sulphuric and phosphoric acids, which communicate respectively a blue and green tinge to the cold core of the hydrogen flame.

660. The following is a list of the substances* which colour the flame, with the colour they impart:

BLUE FLAMES.

(*Consult pars.* 661 and 662.)

Intense blue	Cupric chloride.
Pale clear blue	Lead.
Light blue	Arsenic.
Greenish blue	Antimony.
Blue mixed with green	Cupric bromide.
Blue core colour	Sulphuric acid.

GREEN FLAMES.

(*Consult pars.* 663, 664, and 665.)

Bronze-green border colour	Nitric and Nitrous acids.
„ „ „ „	Ammonic compounds.
„ „ „ „	Cyanogen „
Greenish-blue border colour	Hydrochloric acid.
Green mantle colour	Boracic acid.
Grey yellow-green border colour	Phosphoric acid.
Yellowish-green flame colour	Baric compounds.
Dark green	Iron-wire.
Full green	Copper.
Intense emerald green	Cuprous iodide.
Emerald green, mixed with blue	Cupric bromide.
Pale green	Phosphoric acid.
Intense whitish green	Zinc.

---

* In this list only the more commonly occurring substances are given.

RED FLAMES.

(*Consult pars*. 666, 667, and 668.)

Intense crimson	Strontic compounds.
Reddish purple	Calcic compounds.
Violet	Potassic compounds.
Dark brownish-red border colour and a rose-red mantle colour	Chromic acid.

YELLOW FLAMES.

(*Consult par*. 669.)

Yellow	Sodic compounds.
Feeble brownish yellow	Water.

661. BLUE FLAMES.—$CuCl_2$ gives an azure-blue zone, and $Cu(NO_3)_2$ a pure green flame colour. By the combined observation of both colours, Cu may be distinguished from all other metals which give similar colours. The other flame colouring metals, such as As, Sb, Sn, Pb, Hg and Zn, exhibit, especially in the form of chlorides, more or less intense bluish or greenish mantle colours, which however cannot be advantageously used as reactions for the metals themselves.

662. Sulphuric acid produces a beautiful blue core colour, being reduced to SO_2. The free acid gives the colour when the platinum loop is held in the border of the flame, but a sulphate must be held in the middle of the flame. In the latter case, it is well to dip the test into strong HCl or fluosilicic acid.

663. GREEN FLAMES.—Nitric and nitrous acids give a bronze-green border colour, usually with an orange-coloured border. The test is to be previously dried in the flame, and dipped into a solution of $KHSO_4$, or into dilute HCl, according as we wish to test for nitric or nitrous acid. Ammonic and cyanogen compound give the same bronze-green border, but more faintly. HCl gives a very weak greenish-blue border colour, which lasts for a very short time, and therefore does not deserve attention. The acid is however decomposed, and the Cl may easily be recognised.

664. Boracic acid gives a beautiful green mantle colour, which is so intense that the acid may be recognised in the presence of large quantities of phosphoric acid. Borates are to be decomposed with H_2SO_4. Phosphoric acid gives a grey yellow-green border colour as well as a beautiful green core colour. The dry test is to be dipped into H_2SO_4 and held in the flame in the manner already pointed out, in order to show the border colour. The green core colour is less sensitive, but indispensable in recognising phosphoric acid in the presence of large quantities of boracic acid, and is produced by alternately moistening the test with a solution of fluosilicic acid, and igniting it in the hydrogen flame, until the colour distinctly appears.

665. Ba may be recognised by the yellowish-green flame colour which appears blue green through the green glass. If the green disappears, and a red flame colour makes its appearance, the test is to be repeatedly moistened with HCl, and immediately introduced while wet into the hottest part of the flame. When the blue-green colour is no longer seen, proceed to examine for Ca.

666. Red Flames.—Ca is present when the red flame colour, on evaporating the last portion of HCl, appears siskin green through the green glass. Sr gives in this case a weak yellow. Sr may be recognised by the purple or rose colour which is seen through the blue glass, when the test, after moistening with HCl, is evaporated to dryness in the flame.

667. K gives a grey-blue mantle colour, and a rose-violet flame colour. These colours appear reddish violet through the blue glass, violet through a violet glass, and blue green through a green glass. The test is to be moistened with H_2SO_4, and repeatedly exposed to the flame for a short time.

668. Chromic acid gives a dark brownish-red border colour, and a rose-red mantle colour. The dry test is to be moistened with concentrated H_2SO_4, and held in the border. Chromic oxide gives no colour, and is to be first oxidized to chromic acid by moistening with a solution of sodic hypochlorite and drying.

669. YELLOW FLAMES.—Na gives an orange-yellow flame colour, which in very large quantities appears blue, but in small quantities is invisible through the blue glass. Through the green glass the flame appears orange yellow, even with the smallest quantities; this glass is particularly adapted to the recognition of Na in all its compounds. The test is to be moistened with H_2SO_4, dried and held in the hottest point of the flame.*

670. EXAMINATION OF THE SUBSTANCE IN THE GLASS TUBE CLOSED AT ONE END.—The tube† having been thoroughly cleaned and dried, a *small portion*, in the state of powder, of the substance to be examined is introduced into it, and heated over a spirit or gas lamp, at first gently in order to ascertain whether any VOLATILE SUBSTANCES OF ORGANIC MATTER form part of it; the tube is subsequently heated more strongly with the blowpipe until the glass begins to soften; for the changes consult Table X, and pars. 671, 675.

671. GASES OR FUMES ESCAPE.—"Observe whether they have a colour, a smell, an acid or alkaline reaction, whether they are inflammable, &c.

1st. "*Oxygen.*—The disengagement of this gas indicates the presence of peroxides, chlorates, nitrates, &c. A glimmering slip of wood is relighted in the gaseous current.

2nd. "*Sulphurous acid.*—This is often produced by the decomposition of sulphates, it may be known by its peculiar odour and by its acid reaction.

3rd. "*Hyponitric acid,* resulting from the decomposition of nitrates, especially with oxides of the heavy metals; it may be known by the brownish-red colour of the fumes.

4th.—"*Carbonic acid.*—The evolution of CO_2 indicates the presence of carbonates decomposable by heat. The gas evolved is colourless and tasteless, non-inflammable; a drop of lime-water on a watch-glass becomes turbid on exposure to the gaseous current.

---

* For this description of flame coloration I am indebted to Merz's paper on the subject.

† For the size of the tubes see "Blowpipe," Part III.

TABLE VIII.

EXAMINATION OF THE SUBSTANCE IN A GLASS TUBE CLOSED AT ONE END.

(*See par.* 670.)

	Gases or Fumes Escape. (*See par.* 671.)	
Water condenses on the sides of the tube		Examine whether it has an *alkaline* or *acid* reaction; if the former probably due to NH_3. (*See par.* 672.)
	A sublimate is formed. (*See par.* 673.)	
Volatile Metals. See par. 673 *a.*)	**Arsenic**	The interior surface of the sublimate is crystalline. The odour of garlic is evolved.
	Mercury	Condenses in liquid drops.
	Cadmium	Gives a yellowish-red coating to charcoal when heated on it in the open air.
Volatile Metallic Oxides. (See par. 673 *b.*)	**Antimony Oxide**	Fuses into a yellow liquid before subliming.
	Arsenious Acid	Condenses in white crystals or powder.
	Arsenic Acid	Converted into As_2O_3 and O.

TABLE VIII—*continued.*

Volatile Salts. (See par. 678 *c.*)	AMMONIC SALTS	Volatilized unaltered except when the NH_4 is in combination with a fixed acid.
	MERCURIC CHLORIDE	Melts before subliming.
	MERCUROUS CHLORIDE	Sublimes without previous fusion.
	MERCURY IODIDE	Forms a yellow sublimate.
	MERCURY SULPHIDE	Forms a black sublimate.
	PLUMBIC CHLORIDE	Fuses before it sublimes.
Non-metallic Bodies. (See par. 673 *d.*)	SULPHUR	Forms a yellow sublimate.
	OXALIC ACID	Forms a white crystalline sublimate.

The substance does not volatilize, or not completely.

It LIQUEFIES. (See par. 674 *a.*)

IT BLACKENS (carbonizes). (See par. 674 *b.*)

IT CHANGES COLOUR. (See par. 674 *c.*)

5th. " *Carbonic oxide.*—The escape of this gas indicates the presence of oxalates and also of formates. The gas burns with a blue flame. In the case of oxalates the CO evolved is generally mixed with CO_2, and is therefore more difficult to kindle; in the case of formates the evolution of the gas is attended with marked carbonization. Oxalates evolve CO_2 when brought into contact with MnO_2, a little water, and some concentrated H_2SO_4, on a watch-glass; formates evolve no CO_2 under similar circumstances.

6th. " *Cyanogen.*—The evolution of CN denotes the presence of cyanides decomposable by heat. The gas may be known by its odour, and by the crimson flame with which it burns.

7th. " *Hydrosulphuric acid.*—The escape of H_2S indicates the presence of sulphides containing water; the gas may be readily known by its odour.

8th. " *Ammonia* resulting from the decomposition of ammonic salts, or also of cyanides or nitrogenous organic matters, in which latter case browning or carbonization of the substance takes place, and either cyanogen or offensive empyreumatic oils escape with the NH_3."—Fresenius's 'Chemical Analysis.'

9th. *Nitric acid, fluorine, chlorine, bromine and iodine.*—The detection of these in the preliminary examination is best effected by mixing the substance under examination with rather more than its own weight of *fused* $KHSO_4$, and then heating the mixture in a glass tube closed at one end; before making the examination the student ought to consult pars. *a*, *b*, *c*.

a. Nitric acid.—If a nitrate is present, nitrous fumes are disengaged, the colour of which may be best perceived by looking directly down the neck of the tube, inasmuch as a thicker stratum of the gas is in this way seen.

b. Fluorine.—According to Berzelius the substance ought, for the examination of F, to be mixed with four times its weight of fused $KHSO_4$, and the tube, after the introduction of the mixture, strongly heated with the blowpipe flame until H_2SO_4 begins to be evolved, and in order to avoid too great frothing up, the mass should be heated from the top downwards. If F is present, the tube will be encrusted more or less with silica deposited from the fluosilicic acid gas which passes off. The lower extremity of the tube containing the fused mass is then cut off, and the upper part rinsed out with water and dried with blotting-paper. If much F is present in the substance operated upon, the glass tube will be dull all over its inner surface, but if a small quantity only is present, the corrosion will be only partial.

c. Iodine, bromine and chlorine.—Violent fumes of I are evolved, along with SO_2, on heating a substance containing an iodine compound with $KHSO_4$ in the tube; some of the I is generally deposited as a black sublimate on the upper part of the tube. Br and Cl are in like manner evolved from their compounds.

672. AQUEOUS VAPOURS ARE GIVEN OFF.—The water may have existed either mechanically, or as water of crystallization, or as constitutional water. If the body decrepitates on ignition, the decrepitation is due probably to the presence of an anhydrous salt which contains water mechanically between its crystalline plates and the expulsion of which gives rise to the decrepitation. If the water is present as water of crystallization, the crystalline body will generally fuse during the expulsion, and resolidify after it; some substances swell considerably during the expulsion—borax and alum for example. If the water comes from some decomposable hydrate, the substance will not fuse during its explosion.

673. A SUBLIMATE IS FORMED.—The sublimate may be due to some volatile metal, metallic oxide, volatile salt or non-metallic body.

a. The volatile metals are principally As, Hg, and Cd; these metals form a black or grey sublimate having more or less of a metallic lustre. As is sublimed not only when it exists in its free state, but also from some metallic arsenides, which are decomposed by heat into As and an arsenide containing a less quantity of arsenic; a few arsenites also yield As when heated out of contact with the air. Hg may be sublimed from most of its compounds; if the quantity is inconsiderable, it may only yield a grey sublimate; the globules can sometimes be rendered apparent by touching the sublimate with a glass rod, or on examining the sublimate with a lens. Cd may be sublimed from some of its alloys; it may be recognised by heating it in contact with the air when it becomes converted into the brownish-yellow oxide.

b. VOLATILE METALLIC OXIDES.—Sb_2O_3 first fuses into a yellow liquid, and then sublimes under the form of shining crystalline needles. The sublimate As_2O_3 may either be in the form of shining crystals or in the form of a white powder which the magnifying glass reveals however to be crystalline.

c. VOLATILE SALTS.—*Ammonic salts* form white sublimates; heated with NaHO and a drop of water on platinum foil, they evolve NH_3. $HgCl_2$ begins to melt at a very gentle heat and then sublimes; HgCl sublimes without previous fusion; the sublimate has a yellowish tinge whilst hot, but is perfectly white when cold. HgI_2, which is red, yields a yellow sublimate which becomes red by trituration. HgS gives a black sublimate which acquires a red tint when rubbed. When mercury compounds are mixed with NaHO, and then heated in the tube, a sublimate of mercurial globules will be obtained. $PbCl_2$ first fuses and then sublimes. The sublimate of arsenic sulphide may be easily mistaken for pure sulphur.

d. NON-METALLIC BODIES.—S sublimes in reddish-brown drops, which solidify on cooling, and turn yellow or yellowish brown. The S may be present merely in the state of mixture, or it may be combined with some metal which abandons a portion of it when heated out of contact of the air. *Oxalic acid* yields a white crystalline sublimate attended with thick fumes; the sublimate when heated on platinum foil with a drop of concentrated H_2SO_4 gives rise to a copious evolution of gas.

674. THE NON-VOLATILE MATTER.—The non-volatile portion of the substance may liquefy, carbonize, or merely change colour:—

a. If it liquefies without expulsion of aqueous vapour and resolidifies when the heat is removed, the liquefaction may be due to various substances, as argentic chloride, the alkaline nitrates and chlorates, &c. If by intense heat, O is evolved, and if a small piece of charcoal on being thrown into the fused mass is readily consumed, *nitrates* and *chlorates* are indicated.

b. If it carbonizes organic matter is present. "Carbonization is always attended with evolution of gases (acetates evolve acetone) and water, which latter has an alkaline or acid reaction. If the residue effervesces with acids, whilst the original substance did not show this reaction, organic acids may be assumed to be present in combination with the alkalies or alkaline earths."

c. It changes colour. "From white to yellow, turning white again on cooling, indicates ZnO; from white to yellowish-brown, turning to a dirty light yellow on cooling, indicates SnO_2; if the colour changes from white to brownish red, turning to yellow on cooling, and the body is fusible at a red heat this indicates the presence of PbO; if the colour changes from white, or pale yellow, to orange yellow, or to a deeper and more reddish tint up to reddish brown, becoming pale yellow on cooling, and the body fuses at an intense heat, this indicates the presence of Bi_2O_3; if the colour changes from red to black, turning reddish-brown again on cooling, this indicates the presence of Fe_2O_3; if the colour changes from yellow to dark orange, and the body fuses at an intense heat, this indicates K_2CrO_4, &c."

675. In case of the non-appearance of any of these reactions it must not be always concluded that the above-mentioned bodies are entirely absent; for S and As may be present in such forms that the simple application of heat will either not sublime them or will expel them in combinations which afford none of the distinctive characters of the simple bodies; moreover, two or more of these may be present together in a substance, and afford sublimates having mixed characters, so that the individual elements are difficult to distinguish. Such is frequently the case with As and S, which, together, form a coating on the tube having a metallic lustre at its lower extre-

mity, and passing upwards successively into black, brown, red and finally yellow—these colours being due to combinations of S and As, which are more volatile than As; therefore, the examination of a substance in the glass tube affords frequently no positive indication of the presence of a body, but merely intimates its probable existence, to establish which further investigations are necessary. Such intimations are, however, of importance, as they serve as guides in after-processes.

676. EXAMINATION IN THE OPEN TUBE.—A small particle of the substance, in powder, is introduced into the tube at about half an inch from its extremity, and gradually heated, the tube being held in a slightly inclined position, so that a current of air may pass fully through it. By this means the substance is roasted, or oxidized, and various matters contained in it are volatilized and pass off up the tube.

677. The roasting must be performed slowly, with a gradually increasing temperature, and with a good current of air* passing through the tube, otherwise unoxidized matter may be volatilized and the mineral substance clotted and fused together. If a perfect roasting be required, the substance, after being heated for some minutes in the tube, is shaken out into an agate mortar, remixed and roasted, and this process is repeated until fumes are no longer evolved. (Consult pars. 678 to 681.)

678. Almost all *metallic sulphides* disengage on roasting SO_2; some sulphides yield besides a sublimate of S. SO_2 may be recognised by its odour or by its decolorizing moistened Brazil-wood paper,† a strip of which ought to be introduced in the interior of the raised end of the tube.

679. FLUORINE.—Very minute quantities of F can be detected by the following method:—" Microcosmic salt, which

---

* By inclining the tube more or less, we have the means of regulating the current of air; very little passes through the tube when it is held in a horizontal position, but it becomes more and more active as the tube is held more and more vertically.

† Prepared by moistening slips of fine printing-paper with decoction of Brazil wood.

has been previously fused upon charcoal or platinum, is finely powdered and mixed with some of the substance to be examined also finely pulverized. A portion of the mixture is introduced into an open glass tube, and the blowpipe flame so directed upon it, that a part of the flame passes up the tube. By this means HF is formed (if the substance be free from silica), which passes up the tube and may be recognised both by its peculiar pungent smell and by the mode in which it corrodes the sides of the glass tube, rendering them dull and opaque wherever any moisture condenses. If Brazil-wood paper moistened be exposed to the action of the gases passing up the tube, it will be coloured yellow, affording another indication of the presence of F. If the substance also contains silica, fluoride of silicon will be formed, which also colours yellow moist Brazil-wood paper, and is decomposed by water,* silica being formed, which, as the water evaporates, is deposited on the sides of the tube, and is clearly perceptible either with or without the aid of a lens. If now the tube be washed out with water and dried, it will be generally found corroded by the F, which leaves a dull spot wherever it attacks the glass. As this experiment requires the application of a strong heat, so that the glass tube is frequently softened and bent, thus interfering materially with the success of the experiment, *Smithson* has recommended a piece of platinum foil to be bent into the form of a gutter and inserted to about half its length into the glass tube; the mixture of the fused microcosmic salt and the substance under examination is laid upon the projecting part of the platinum, and the flame so directed upon it that the products of combustion pass up the tube. This arrangement has the advantage that the fused substance does not come in contact with the glass tube, and the inconveniences attending the fusing and softening of the glass are altogether avoided.

680. A sublimate may be formed in the second operation when none has been formed in the first, as Bi_2O_3 will be

---

* Water will be present owing to the products of the combustion of the lamp passing up the tube.

formed when the Bi_2S_3 or a bismuth alloy (scarcely any sublimate is produced on roasting Bi itself) is present in the substance under examination, and $PbSO_4$ will be formed if PbS is present; in like manner, As_2O_3 and Sb_2O_3 will be formed if an arsenide or an antimonide is present. If the fumes formed have an odour of garlic it shows the presence of As.

681. All the sublimates which are formed by oxidizing substances in the open tube are white, but the coloured substances which are volatilized in the closed tube are still more easily volatilized in the open tube; for it need scarcely be observed that most of the reactions produced in the closed tube are also produced in the open one.

682. EXAMINATION ON CHARCOAL.—Most of the reactions described in pars. 670 to 679 are also produced on the charcoal; but only those reactions which are special to this operation are noticed in Table IX and text.

683. In addition to the points which require to be attended to, as pointed out in the table, it should be particularly noticed whether the substance disengages a peculiar odour, as As and S might be detected by the odours they produce;* and it should also be noticed whether the substance fuses; the oxides and acids which fuse are the oxides of Sb, Bi, Pb, and Cu. "Most metallic sulphides fuse when heated before the blowpipe upon charcoal, and this effect often takes place with sulphides of those metals, whose oxides are infusible; but many of these sulphides become rapidly oxidized during the operation, and exhale an odour of SO_2 in the same way as when heated in the open tube, and are thus converted into metallic oxides. Most metals fuse before the flame of the blowpipe; and all of them, except those called noble, are subsequently oxidized by the exterior flame." After this examination is complete, the substance must still be retained on the charcoal for the examination with $Co(NO_3)_2$.

684. TREATMENT WITH COBALTIC NITRATE.—No explanation beyond that given in Table X is required.

---

* It must be remembered that charcoal becomes, on exposure to the blowpipe flame, covered with a *bluish-white ash.*

TABLE IX.

EXAMINATION ON CHARCOAL. (See par. 682.)

If deflagration ensue, the presence of a *chlorate* or *nitrate* is indicated.

Substances which volatilize or pass off in vapour.	***Substances which are not volatilized.***		
MERCURY, ARSENIC, CADMIUM, ANTIMONY, ZINC, AMMONIA, SULPHUR, and LEAD partly.	SILVER, COPPER, BISMUTH, LEAD, TIN, GOLD, PLATINUM, COBALT, NICKEL, MANGANESE, IRON, ALUMINUM, CHROMIUM, BARIUM, STRONTIUM, CALCIUM, MAGNESIUM, SODIUM, POTASSIUM, SILICA, &c.		
Colour of the different Sublimates.	Substances which yield *coloured incrustations.*	Substances which are *infusible, but become luminous.*	Substances which *fuse, or run into the charcoal.*
MERCURY, ZINC, AMMONIA . White. ANTIMONY, white, imparting a greenish-blue colour to the flame. CADMIUM . . . . Red brown.	LEAD, } Yellow. BISMUTH, } Yellow.	ALUMINA, BARYTA, STRONTIA, LIME, and MAGNESIA, *and their salts.*	SALTS OF THE FIXED ALKALIES.

685. EXAMINATION WITH SODIC CARBONATE ON CHARCOAL.—The substance (in powder) under examination is mixed with an equal quantity of Na_2CO_3, and the mixture is made into a paste with a drop of water. After it has been dried at a moderate heat, it is exposed on the charcoal to the reducing flame of the blowpipe, the oxidizing flame spreading over the charcoal. (See Table X, and pars. 686 to 699.) Should no reduced metal make its appearance, after exposure for two or three minutes to the flame, a little KCN may be added, and the experiment continued for two or three minutes longer. Many of the metallic arsenides and sulphides require to be carefully roasted, and thus deprived of their As and S, and the metals themselves oxidized, before they can be reduced by Na_2CO_3; in this case, the residue which remains from the open-tube experiment can be employed. It must be remembered, however, that Cd as well as S and As may have been expelled by the roasting.

686. The metals which can be reduced by this means, besides Au, Pt, and Ag, are Pb, Sb, Sn, Cu, Zn, Bi, Ni, Co, Fe, Cd, As, and Hg. "Au, Ag, Cu, and Sn compounds, yield metallic beads, but no incrustations; Fe, Ni, Co, and Pt compounds give neither beads nor incrustations; Bi, Pb, and Cd compounds produce a yellow or brown deposit on the charcoal; Sb and Zn give a white incrustation;* As may easily be recognised by its odour."

687. If a globule has been obtained, it is necessary to ascertain whether it is malleable or brittle: "for this purpose, it is allowed to cool perfectly, and carefully removed with a pair of tweezers. Having been placed upon a little anvil,† and struck

---

* The ash of the charcoal may sometimes be mistaken by beginners for a sublimate, but it may be distinguished from such by remaining unaltered before the inner flame.

† The anvil is a small block of hardened steel about two inches square and three quarters of an inch thick, polished upon one or more of its faces. The hammer is made of hardened steel, one face must be square with sharp edges, for trying the malleability of substances, and the opposite end should be bevelled off like a chisel to detach small fragments of minerals, &c.

TABLE X.

BLOWPIPE OPERATIONS.

Heat the substance on **Charcoal**, with the blowpipe flame; then moisten it with a solution of $Co(NO_3)_2$; again strongly heat it in the *outer flame*. (See par. 684.)		Mix the substance with Na_2CO_3, and expose the mixed mass to the inner blowpipe flame, on **Charcoal**. (See pars. 685 to 699.)		Heat the substance before the blowpipe on **Platinum Wire**, with a bead of **Borax**. (See pars. 700 and 701.)	
Substances which yield *coloured masses* when thus treated.		Oxides and other Combinations of the Metals which can be reduced to the *metallic state*.		Substances which give *coloured beads*.	
		Oxide of	*Character of the Metal.*	*In the outer flame.*	
Zincic Oxide	Green.	**Bismuth**	Brittle.	**Copper**, **Cobalt**,	Blue.
Alumina, **Silicic Acid**, **Phosphates**,	Blue.	**Antimony**	Brittle; volatilizes in white fumes, yielding an incrustation.	**Nickel**	Reddish.
		Silver	Malleable; very white.	**Iron**	Yellow.
		Tin	Malleable.	**Manganese**	Amethyst.
		Lead	Malleable, very.	**Chromium**	Green.
Magnesia	Pink.	**Copper**, **Gold**,	Well known colours of the metals.	*In the inner flame.*	
Stannic Oxide	A bluish-green colour.	**Nickel**, **Cobalt**, **Iron**,	These three are reduced, but yield no metallic beads; they are rendered magnetic, and can therefore be at once distinguished from the rest.	**Copper**	Red.
				Cobalt	Blue.
				Nickel	Grey.
				Iron	Green.
				Manganese	Colourless.
				Chromium	Green.

To discover the reduced metal, remove the fused mass from the charcoal, and grind it up in a small mortar with water; allow it to stand a minute, and then pour off the water and the suspended matter in it, and continue to repeat the process until the metal remains at the bottom of the mortar, perfectly free from charcoal, &c. If it is brittle, it will be in the state of very small spangles; if malleable, it will have adhered to the mortar or pestle, or a portion of it, whilst the rest may be in large spangles.

with a small hammer—or, if these two blowpipe instruments are not at hand, upon the bottom of a strong mortar—and struck sharply with the pestle, if brittle, it of course falls to powder (as in the case of Sb); if semi-malleable, it flattens out, at the same time breaking into several pieces (as with Bi); and if fully malleable, flattens out without breaking (like Pb).*

688. "*The globule obtained is malleable.*—Pb (makes a black streak upon paper); a yellow incrustation is formed upon the charcoal. Sn; a slight white incrustation. Cu (known by its colour). Ag.

689. "*The globule is semi-malleable.*—Bi; a yellow incrustation.

690. "*The globule is brittle.*—Sb; abundant white incrustation.

691. "*If no metallic globule* is obtained, but shining *metallic spangles* are observed after levigation; probably Sn, Sb, or Cu."

692. MAGNETISM.—To ascertain whether the reduced metal is magnetic, an ordinary steel magnet must be presented to it; if any of the metallic particles are magnetic they will adhere to it. The trial may be made with far more delicacy by bringing the metallic particles near a magnetic needle which is supported on a centre, on which it turns.

693. Only one mineral, magnetic oxide of iron, possesses magnetic *polarity* and *attraction*, all other minerals, which are attracted by the magnet, possess attraction only. The magnetic character serves to distinguish a few of the mineral species, which otherwise have very close resemblances; especially, magnetic iron ore from specular iron, and magnetic pyrites from common pyrites.

694. Many minerals become attractable by the magnet, only after undergoing the high heat of the blowpipe; this is the result of a partial decomposition.

695. CUPELLATION.—This is the process of separating gold

---

* To prevent the fragments from dispersing from the striking they may be folded in a piece of thin paper, the corner of which may be held during the operation.

and silver from other substances by heat, and obtaining them in a state of purity. The following is Berzelius' method:

696. "A small quantity of bone-ashes (in powder) is to be taken on the point of a knife, moistened with the tongue, and kneaded in the palm of the left hand, with a very little soda into a thick paste. A hole is then made in a piece of charcoal, and filled with the paste, and its surface smoothed by pressure with the agate pestle. It is then to be gently heated by the blowpipe till perfectly dry (the soda only assists the cohesion, and may be omitted). The assay,* previously fused with *pure* lead, is placed in the middle of this little cupel, and the whole heated by the exterior flame. When the operation is finished, the precious metals are left on the surface of the cupel. This experiment is so delicate that grains of Ag, visible to the naked eye, and, indeed, such as may be collected by the forceps and extended under the hammer, may in this way be extracted from the lead met with in commerce.

697. "If the button obtained by cupellation does not possess the colour of Au, but appears white, the quantity of Au is less than that of Ag, in which case, the button should be placed in a porcelain capsule, a few drops of HNO_3 poured on it, and the capsule heated over the lamp.

698. "If the button does not contain more than a fourth part of its weight in Au, it becomes completely black, and then decomposes, the Ag being dissolved, while the Au remains in black flakes. When the silver button contains more than a fourth of its weight of Au, it is blackened, but the Ag is not dissolved. It is neither blackened nor dissolved, if the proportion of Au to Ag is nearly equal; in this case the button must be melted with twice its bulk of pure Ag, on charcoal, and again heated with HNO_3, by which the mass becomes black, and dissolves; the pure Au being left behind."

699. If the substance fuses into a transparent glass with the Na_2CO_3, it shows the presence of silica, par. 458.

700. TREATMENT WITH BORAX.—To obtain a bead of borax,

---

* It would be better to roast the substance under examination with Na_2CO_3 on charcoal before assaying it with the pure lead.

one end of the platinum wire is bent into a small hook. This is heated in the blowpipe flame, and then dipped into the borax; a small portion of the borax will adhere to it; and this being fused in the flame, and, while hot, dipped again into the powdered borax, a fresh quantity will adhere, which is fused as before; and this continued until a bead of the requisite size is obtained. A great many metallic oxides dissolve in borax, forming coloured glasses. If any metallic arsenides or sulphides are present, it is necessary to roast the substance in the way previously described (676) before making the examination with borax; and it is frequently advantageous, before roasting the powdered substance, to mix it with a little powdered charcoal, so as to prevent the formation of sulphates and arseniates.

701. While the bead of borax is still hot, it is touched with a small quantity of the powder of the substance under examination, and that which adheres is fused into it. The operator must then observe—1st, whether the substance is soluble or insoluble in borax; and 2nd, the colour of the borax bead in (1) the oxidizing flame, and (2) in the reducing flame, both in the hot and in the cold state. In performing this experiment, care must be taken not to dissolve up, in the first instance, too large an amount of the oxide or other substance under examination. If a small quantity afford no distinct reaction, more may be easily added. If, however, the colour of the bead is too intense to be clearly distinguished, the bead may be jerked off the wire, and that which still adheres fused up with a fresh quantity of borax, by which a paler and more transparent glass will be obtained.

702. EXAMINATION IN THE PLATINUM FORCEPS.—"If the operator has convinced himself by a preliminary experiment that the substance under examination does not, when heated, attack platinum,* a small splinter of it is to be taken between the platinum forceps, and subjected to the oxidizing flame; but if the substance is very fusible, a piece of platinum wire, hooked at one end, may be used instead of the forceps. If,

---

* Platinum cannot be employed when compounds of the easily reducible metals, as Ag and Pb, are present.

however, the substance be one which exerts a chemical action on platinum, and would therefore injure the forceps or wire, charcoal must be employed as the support.

703. "In order to test the fusibility of a mineral, a small splinter, having a sharp edge or point, should be broken off and held in the forceps at a short distance beyond the point of the inner blue flame, so that the sharp edge is strongly heated. If a gas flame be employed, the mineral must be held somewhat further from the point of the blue flame than is necessary in the case of an oil-lamp, in order to prevent any reduction taking place, which would materially interfere with the results. If a powdered substance is to be tested, or one which decrepitates when heated, and which must therefore be previously pulverised, the following process may be resorted to:—A small quantity of the powder is made into a paste with water, and spread upon a piece of charcoal; it is then dried, and strongly heated with an oxidizing flame, it will then (generally) cohere sufficiently to allow of its being taken up between the forceps and tested in the usual manner. Care must be taken that the substance, if a fusible one, and one which acts upon platinum, does not fuse upon the platinum points of the forceps.

704. "Of the metallic oxides, the following only are fusible in the oxidizing flame, viz. the oxides of Cu, Pb, Sb, and Bi. Metallic sulphides are, with few exceptions, readily fusible under the blowpipe flame; these exceptions are ZnS and MnS."

705. "Of the simple silicates, *i. e.* silicates with a single base, those of the alkalies are most fusible. The silicates of Ca and Mg are with a few exceptions practically infusible. Aluminic silicates are infusible.

706. "Of the iron silicates those of ferrous and magnetic oxide are very fusible, but the ferric silicates are practically infusible. Consequently, under the blowpipe flame, the fusibility of an iron silicate much depends upon whether it be submitted to the oxidizing or the reducing flame; for the ferric silicates infusible in the former become fusible and magnetic in the latter. If, therefore, a substance be infusible, or only

very slightly fusible in the oxidizing flame, it may afterwards be submitted to the extremity of the reducing flame, since many substances infusible in the former become fusible on undergoing a partial reduction.

707. "The fusibility of a compound silicate, *i. e.* a silicate containing two or more bases, depends upon that of the simple silicates of which it is composed, but is generally greater than the mean of these latter. Thus many calcic and magnesic silicates, and calcic and aluminic silicates, are more fusible than any of the simple silicates which enter into their composition.

708. "According to their relative fusibility, minerals may be classified as follows:

I. Readily fusible to a bead.
II. With difficulty fusible to a bead.
III. Readily fusible on the edges.
IV. With difficulty fusible on the edges
V. Infusible.

709. "In testing the fusibility of a mineral substance, it should be noticed whether, if fusible, a clear or opaque bead is obtained; also, whether the substance changes colour, becomes magnetic, or exhibits any phenomena of intumescence, ebullition, &c., all of which are useful characters in indicating the nature of the mineral."

710. "The degree of fusibility is a very important point to ascertain, when the examination in question refers to the native *combinations of silica* and certain other *minerals*, for this characteristic feature displayed by the blowpipe is often the only one by which we may distinguish those which consist of earths, and which contain no notable quantities of metallic oxides, properly so called. Amongst the minerals most frequently met with, the following are infusible:

Quartz,
Corundum,
Tourmaline (both that which contains alumina and even that which contains soda),

Zircon,
Cyanite,
Phenakite,
Leucite,
Talc,

Pyrophyllite,
Apatite,
Gehlenite,
Apophyllite,
Staurotide,
Refractory clays,
Aluminic hydrate,
Magnesic hydrate,
Aluminic sulphate,
Calcic carbonate,
Magnesic carbonate,
Zincic carbonate,
Allophane,
Spinel,
Pleonaste,
Gahnite,
Olivine,
Cerite,
Cymophane,
Gadolinite (which, being heated, becomes suddenly luminous, as if it caught fire),
Vitreous tin,
Rutile,
Titanic iron,
Tantalite,
Turquoise,
Titaniferous oxide of iron,
Chrome iron,
Native oxides of iron,
Yttrotantalite,
Dioptase,
Chondrodite,
Topaz.

711. "Amongst those which are almost infusible and only become rounded at the edges, the following may be named:

Felspar,
Albite,
Petalite,
Labradorite,
Anorthite,
Nepheline,
Tubular spar,
Pyroxène (which contains much magnesia),
Epidote (which intumesces by the first impression of the heat)
Euclase (which intumesces by the first impression of the heat),
Emerald,
Titanite,
Sodalite,
Calcareous Scheelin,
Meerschaum,
Soapstone,
Serpentine,
Mica (some species, especially those found in granite),
Dichroite,
Heavy spar,
Celestine,
Gypsum,
Apatite,
Fluor spar.

Table of Volatile Elements which

	Metallic film.	Oxide-film.	Oxide-film with stannous chloride.	Oxide-film with stannous chloride and soda.	Oxide-film with silver-nitrate and ammonia.
Te	Black; thin part brown.	White.	Black.	Black.	Yellowish white.
Se	Cherry-red; thin part brick-red.	White.	Brick-red.	Black.	White.
Sb	Black; thin part brown.	White.	White.	White.	Black; insoluble in ammonia.
As	Black; thin part brown.	White.	White.	White.	Lemon-yellow or reddish-brown; soluble in ammonia.
Bi	Black; thin part brown.	Yellowish white.	White.	Black.	White.
Hg	Grey non-coherent thin film.				
Tl	Black; thin part brown.	White.	White.	White.	White.
Pb	Black; thin part brown.	Yellow-ochre colour.	White.	White.	White.
Cd	Black; thin part brown.	Blackish brown; thin part white.	White.	White.	White; in the thin parts turns bluish black.
Zn	Black; thin part brown.	White.	White.	White.	White.
Sn	Black; thin part brown.	Yellowish white.	White.	White.	White.

can be reduced as Films.

Iodide-film.	Iodide-film with ammonia.	Sulphide-film.	Sulphide-film with ammonium-sulphide.	
Brown; disappears for a time on breathing.	Disappears altogether on blowing.	Black to blackish brown.	Disappears for a time.	Elements whose reduction-films are scarcely dissolved in dilute nitric acid.
Brown; does not wholly disappear on breathing.	Does not disappear on blowing.	Yellow to orange.	Orange, and then disappears for a time.	
Orange-red to yellow; disappears on breathing.	Disappears altogether on blowing.	Orange.	Disappears for a time.	
Orange-yellow; disappears for a time on breathing.	Disappears altogether on blowing.	Lemon-coloured.	Does not disappear.	
Bluish brown; thin parts pink; disappears for a time on breathing.	Pink to orange; chestnut-coloured when blowing.	Burnt-umber-colour to coffee-coloured.	Does not disappear.	Elements whose reduction-films are with difficulty dissolved in dilute nitric acid.
Carmine-coloured and lemon-yellow; does not disappear on breathing.	Disappears for a time on blowing.	Black.	Does not disappear.	
Lemon-yellow; does not disappear on breathing.	Does not disappear on blowing.	Black; thin parts bluish grey.	Does not disappear.	
Orange-yellow to lemon-colour; does not disappear on breathing.	Disappears for a time on blowing.	Brownish red to black.	Does not disappear.	Elements whose reduction-films are instantly dissolved in dilute nitric acid.
White.	White,	Lemon-coloured.	Does not disappear.	
White.	White.	White.	Does not disappear.	
Yellowish white.	Yellowish white.	White.	Does not disappear.	

708. "The following are fusible:

Zeolites (most of them intumesce),
Spodumene (which intumesces),
Mejonite (which froths up before fusing),
Elæolite,
Amphibole (most of which boil up whilst in fusion),
Pyroxène (those which contain no excess of magnesia),
Idocrase (intumesces in fusing),
Garnet,
Cerine,
Orthite (boils in fusing),
Ferruginous Scheelin,
Boracite,
Hydroboracite,
Datholite,
Botryolite,
Cryolite,
Mica (several species, especially those which contain lithia),
Tourmaline (those which contain potash),
Axinite (intumesces whilst fusing),
Amblygonite,
Lazulite,
Haüyne,
Nosin,
Eudialyte,
Pyrosmalite."—*Rose's Manual of Analysis.*

712.—*Bunsen's flame reactions.*—Almost all the reactions which can be performed by means of the blowpipe may be accomplished with far greater ease and precision in the flame of the non-luminous gas-lamp.* This flame, moreover, possesses several peculiarities which render it available for reactions, by which the smallest traces of many substances occurring mixed together can be detected with certainty when the blowpipe, and even still more delicate methods fail. The method of examination of the various parts of the flame for these flame reactions is described in pars 1167 to 1173, and the special behaviour of the bodies themselves has been described under the head of their special properties; we shall, therefore, only here give a table (given by Bunsen in his paper on flame reactions) of the volatile elements which can be reduced as films. This table contains some of the rarer elements which are not given in the book.

---

* See description of Bunsen's lamp in Part III.

713. *When the student has completed the preceding preliminary experiments, he will be able to arrange the substance under examination* UNDER ONE OF THE THREE FOLLOWING DIVISIONS:

714. THE SOLID IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER. See par. 717.

715. THE SOLID IS NEITHER A PURE METAL NOR AN ALLOY, BUT CONTAINS ORGANIC MATTER. See par. 731.

716. THE SOLID IS EITHER A PURE METAL OR AN ALLOY, See par. 737.

717. THE SOLID IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER.

718. Before a solid can be acted upon by reagents, it must be brought into a state of solution. For this purpose it is submitted to the action of different fluids, and the one in which it dissolves is termed its solvent. The solvents employed in qualitative analysis, are water, HCl, HNO_3, and aqua regia. Water, when it can be employed, is always to be preferred.

719. The student must particularly guard against adding too much of the solvent, especially if it be an acid. To avoid this, he must add it in small quantities at a time, and apply heat after each addition. The substance should, before being submitted to the action of solvents, be reduced to the state of a very fine powder, and fifteen or twenty grains employed for the analysis. The whole of the substance must, however, never be employed, but always a portion kept in case of any unforeseen accident, or for confirmatory experiments. In ascertaining in what liquid the substance is soluble, the student ought only to employ about three or four grains of the

substance; after he has ascertained the solvent he can then dissolve up the fifteen or twenty grains for the analysis.

720. The powdered substance is boiled in ten times its amount of water. *It all dissolves.*—Examine it according to par. 640. *A portion remains undissolved.*—Filter a few drops of the liquid, and evaporate them to dryness on platinum foil. If a large residue remains on evaporation, the whole of the solution must be filtered, and examined according to par. 640. The insoluble residue, after being well washed with boiling water, must be examined according to 721. If no residue remains on evaporating the aqueous solution, or at all events a very slight one, pour the remainder of the water off, and treat the insoluble substance according to 721.

721. The substance which was partly or entirely insoluble in water, is boiled in dilute HCl, and if not soluble in dilute, then in concentrated HCl.* *It all dissolves.*—Treat the fifteen or twenty grains in the same way and proceed with the examination for the bases in the usual way, and for the acids according to 547.† *A portion remains undissolved.*—Ascertain if anything has dissolved, by evaporating a portion of the fluid to dryness on platinum foil. Should this be the case, place the tube, with its contents, on one side, and proceed with the next experiment.

722. A fresh portion of the original substance is boiled in HNO_3. *The substance dissolves.*‡—Remove as much of the free acid as possible by evaporation; dilute the concentrated solution with water, and then proceed with the examination for the bases in the usual way, and for the acids according to

---

* If HCl causes any effervescence, the evolved gas must be examined for CO_2, H_2S, and HCN, as directed under these acids.

† If the substance is silicate decomposable by HCl, treat it according to par. 455.

‡ If the substance dissolves with the separation of a light-yellow coloured mass of sulphur, it points out the presence of a sulphide. When HNO_3 is employed as the solvent, as much of the free acid as possible ought to be removed by evaporation, before passing H_2S through the solution, as they decompose each other, the decomposition being attended with the separation of a large amount of sulphur.

547. *It does not dissolve.*—Allow it to settle; pour off one half the acid, add a like quantity of concentrated HCl, and again boil. If a portion still remains undissolved, return to the strong HCl mixture (721): filter, and analyse the filtrate in the usual way. The residue insoluble in acids, after being well washed, must be treated according to 723.

723. The usually occurring substances, which are insoluble in water and acids, are the BARIC, STRONTIC, CALCIC, and PLUMBIC SULPHATES, ALUMINA, FERRIC OXIDE, and their *phosphates*, the ARGENTIC and PLUMBIC CHLORIDES, CALCIC FLUORIDE, SILICATES, SILICA, and SULPHUR.

724. A small portion of the residue, insoluble in water and acids, is heated on a slip of platinum foil. If SO_2 is evolved along with the volatilization of the whole of the substance, sulphur only can be present. When other substances are present, add to another small portion a drop of $(NH_4)_2S$. If the colour remains white, Ag, Pb, and probably Fe, are absent.

725. A small quantity of the dry residue, in the state of a very fine powder, is mixed with four times its weight of a mixture of equal parts Na_2CO_3 and K_2CO_3. The mixed mass is placed in a platinum crucible,* and heated over a gas lamp for about half an hour; or, what is still better, the platinum vessel is placed within a Hessian crucible containing a little $MgCO_3$, and exposed to a full red heat, for the same length of time, in a furnace. The magnesic carbonate is employed to prevent the platinum from coming in contact with the Hessian crucible.

726. On cooling, the fused mass is boiled with water, and filtered. The filtrate is to be examined for the *acids* and *alumina*, the residue for the *bases*.

727. *Examination of the filtrate.*—To one portion of the filtrate add HCl until the solution is distinctly acid; evaporate to dryness, and ignite until acid fumes are no longer evolved.

---

* The compounds of the easily reduced metals, such as Ag, Pb, &c., must not be fused in platinum vessels, as they form alloys with that metal, which greatly injures or altogether destroys the platinum vessel: porcelain crucibles must therefore be employed in such cases.

To the dried mass add dilute HCl and boil; if a residue remains, silicic acid is present. To the filtrate from the silica add NH_4HO in excess, and then warm the solution; if a precipitate is formed, it must be due either to alumina or its phosphate. After having filtered and washed the precipitate, examine it for alumina and aluminic phosphate according to Table V. In the filtrate from the alumina precipitate, or in the solution which has failed to give a precipitate, test for phosphoric acid by adding NH_4Cl, and then $MgSO_4$. Acidulate another portion of the original filtrate with HCl, and examine for sulphuric acid by adding $BaCl_2$. Another portion must be acidulated with HNO_3, and tested for chlorine by $AgNO_3$. To detect fluorine, an examination must be made according to 462 or 463.

728. *Examination of the residue.*—After having removed all the substances soluble in water, by repeated washings, dissolve the residue, if Pb and Ag are absent, in HCl, and proceed with the analysis in the usual way. If the residue does not completely dissolve in the acid, and the two metals just named are absent, it shows that a portion of the substance has not been decomposed. When this is the case, filter off, and examine the filtrate.

729. When the fixed alkalies are to be looked for in the insoluble residue, another portion, in fine powder, must be mixed with about four times its weight of $BaCO_3$, and fused in a platinum crucible, in the manner already described. On cooling, the fused mass is digested with dilute HCl, and filtered. The filtrate is evaporated to dryness, and ignited; the dry residue must be treated with water, and again filtered. The filtrate, after being freed from iron oxide, alumina, baryta, lime, and magnesia (if present) must be evaporated to dryness, to expel the ammonic salts which have been employed in their precipitation; if a residue remains, it must be examined for K and Na.

730. Bloxam has proposed to fuse insoluble substances by mixing them with a deflagrating mixture. A great saving of time and labour is thus effected by causing the heat to be

applied *inside* the mass to be fused. The following is the process:—5 grains of the substance are intimately mixed with 10 grains of dried Na_2CO_3 and 70 grains of the deflagrating flux, composed of charcoal* and nitre in the proportion of one part by weight of the former to six of the latter. The mixture is placed in a *thin* porcelain dish, or clean iron tray, and a lighted match applied to the centre of the heap. The deflagration is completed in two or three seconds, and a well-fused mass remains. This is easily detached from the cooled dish (in which a little unburnt charcoal may be left), and boiled with water, being occasionally stirred with a glass rod. Two or three minutes always suffice for the extraction of the soluble portion, which is then filtered off, and examined for acids and for such bases as are compatible in solution with the alkaline carbonates (par. 727). The residue left by water, after having been washed, is treated with acids, and examined in the usual way (par. 728). A little charcoal is generally left undissolved by acids, and with it any of the substances which may have escaped decomposition. If it be thought necessary, the dried residue may be ignited until the charcoal is consumed, and the incombustible portion examined.

731. THE SOLID SUBSTANCE UNDER EXAMINATION IS NEITHER A PURE METAL NOR AN ALLOY, BUT CONTAINS ORGANIC MATTER.

732. The presence of fixed organic matter † interferes with the detection of many substances. Thus, in the presence of

---

* The charcoal should, of course, be chosen so as to yield a very small proportion of ash, and must be reduced to a fine powder: the charcoal from the powder-mills is most suitable for the purpose. The nitre must be chemically *pure*.

† Organic substances are termed *fixed* when they cannot be distilled or volatilized without decomposition. The organic matter ought to be tested for nitrogen; for this purpose it is mixed with caustic potash in powder or with soda-lime, and the mixture heated in a test-tube, when, if it contains nitrogen, NH_3 will be evolved.

tartaric acid, which is a fixed organic acid, aluminic, chromic, iron, and many other metallic oxides, are not precipitated by the alkalies ; alkaline citrates prevent the precipitation of acids, by bases, with which the acids form insoluble salts under ordinary circumstances; a soluble baric salt will not produce a precipitate, even in a solution of a sulphate, if an alkaline citrate be present, unless the sulphate is present in the proportion of three or more equivalents for every one of the citrate. Soluble plumbic and strontic salts produce, likewise, no precipitate in solutions of sulphates in the presence of citrates, the citrates interfere with the precipitation of a large number of substances, Mn, for instance, is not precipitated from its solutions by ammonic sulphide.* It is therefore necessary, after precipitating the fifth and sixth groups by HCl and H_2S, to destroy the fixed organic matter, when it is present, which will have been ascertained in the preliminary examination. For this purpose, the filtrate from the H_2S precipitate, or the solution which has failed to give a precipitate with this reagent, is evaporated to dryness and ignited † until all the organic matter has been destroyed, the residue must then be dissolved in water or acids as directed at par. 718 ; and then examined for the 4th, 3rd, 2nd, and 1st groups of basic substances in the usual way. The examination of the acids must be conducted as directed at par. 720, and following pars.

733. Sometimes we are obliged to have recourse to the following method for destroying the organic matter, especially in the case of liquids and solids which have to be examined for *poisons*. The solid or liquid is placed in a porcelain dish, and to it is added pure concentrated HCl, about equal in weight to the *dry* solid present, and then, if required, water to make the mass of a thin pasty consistence, the dish is placed on the

---

* Spiller on the Influence of Citric Acid on Chemical reactions. Quarterly Journal of the Chemical Society of London, vol. x.

† Many substances, especially aluminic and the iron oxides, after ignition dissolve with very great difficulty even in the concentrated mineral acids. The residue may therefore require protracted boiling in acids, although the original substance dissolved in water or dilute acid very readily.

water-bath, and small portions of pure potassic chlorate are added every five minutes or so, stirring constantly at the same time the contents of the dish; the addition of the potassic chlorate is continued until the mixture is perfectly fluid and of a light-yellow colour; when this is attained we add 20 or 30 grains more of the $KClO_3$, and continue the heat until the liquid ceases to smell of chlorine; the mixture is then filtered through paper or linen, the residue thoroughly washed, and the wash-water concentrated over the water-bath, and then added to the filtrate; the filtrate is examined as directed in the next par. The residue must be examined for AgCl, $PbSO_4$, and SnO_2 as directed at par. 723.

734. The filtered liquid is placed in a flask and kept at a temperature between 60° and 70° C., and washed H_2S transmitted through it for about twelve hours, it is then allowed to cool, and during the cooling the transmission of the gas through it is continued; it is then covered over with paper and placed in a moderately warm place, and allowed to stand for twenty-four hours; if at the end of that time it has only a faint odour of H_2S, the gas is again passed through it to excess, and it is again allowed to stand until the odour of H_2S has again nearly disappeared; the precipitate is then collected upon a filter and washed until the washings are quite free from Cl; the filtrate is examined for the members of the 4th and 3rd groups.

735. The precipitate contains, besides any metals that may be present, organic matter and sulphur; if the analysis has been instituted, not for the examination of the poisonous metals, the precipitate can be examined in the usual manner; but if the examination is made to ascertain whether any of the poisonous metals are present, it may be conducted in the following manner:—Digest the precipitate for some time in NH_4HO, the As_2S_3 dissolves, and the other sulphides remain undissolved; filter off and evaporate the filtrate along with the wash-water to dryness on the water-bath, the As_2S_3 will remain; it is generally of a brown colour, from the presence of organic matter which has been dissolved by the NH_4HO. Examine the

precipitate according to the electrolytic method (273), or according to the method described in par. 260.

736. The precipitate insoluble NH_4HO, after it has been thoroughly washed, is digested in yellow $(NH_4)_2S$; it is then filtered, and the filtrate, along with the wash-water, is evaporated to dryness over a water-bath; the residue is examined for Sb_2S_3 by the usual tests. Treat the sulphides insoluble in $(NH_4)_2S$ according to par. 294.

737. THE SUBSTANCE UNDER EXAMINATION IS A PURE METAL OR AN ALLOY.

738. Nitric acid behaves with metals in the following manner: —Au and Pt are neither dissolved nor altered in the least degree by it. Sn and Sb are converted by it into oxides, which do not dissolve in or combine with an excess of the acid. The other metals are oxidized and converted by it into soluble nitrates. On account of the different behaviour, therefore, which HNO_3 exhibits with the metals, it is usual to employ it as the solvent of alloys, &c.

739. To the metal or alloy under examination, which is placed in a small flask, is added HNO_3 of sp. gr. 1.20, and heat applied. One of the three following cases will then occur: —1. Complete solution takes place. 2. A white insoluble substance separates. 3. A metallic residue remains. Each of the three cases is considered separately in detail.

740. 1. *If complete solution ensues*, Au, Pt,* Sn, and Sb† must be absent. After removing the greater part of the free acid by evaporation, dilute the solution with water,‡ and proceed with the analysis in the regular way. Hg, if present, will be found in the mercuric state.

741. 2. *If a white insoluble substance separates*, Sn or Sb is

---

* Alloys of Ag and Pt, with the latter metal present in small proportion only, dissolve in HNO_3.

† Very minute traces of Sb are often completely dissolved by HNO_3.

‡ If the solution becomes turbid on the addition of water, it indicates the presence of Bi.

indicated. After removing the greater part of the free acid by evaporation, dilute the solution with water, filter, and proceed with the filtrate in the ordinary way. The precipitate, after being well washed with water, is treated with a hot concentrated solution of tartaric acid. If it all dissolves, Sn is absent. The presence of Sb is confirmed by H_2S producing in the tartaric acid solution, to which HCl has been added, an orange-red precipitate. If the whole of the *insoluble substance* does not dissolve in tartaric acid, the solution is filtered. The filtrate is examined for Sb by the method just stated. The residue, after being well washed, is mixed with Na_2CO_3 and KCN, and exposed on a charcoal support to the inner blowpipe flame. If Sn is present, ductile metallic grains will be obtained.

742. 3. *If a metallic residue remains*, Au or Pt is indicated. After removing the greater part of the free acid by evaporation, dilute the solution with water, filter, and examine the filtrate in the usual way. The metallic residue is dissolved in aqua regia. One portion of the solution is tested for Au according to 284. The other portion is tested for Pt according to 287.

743. Answers to the following exercises must be written out.

EXERCISES.

175. If you had such a mixture as the following, whether would it be more advantageous to treat it, 1st with water until all the soluble matter was removed, and then with HCl, or to treat it at once with HCl: what difference would there be between the two modes of treatment:—Na_2SO_4, KNO_3, NH_4Cl, $BaCO_3$?

176. Whether would it be better to treat such a mixture as the following, 1st, with water, and, 2nd, with HCl, or to treat it at once with HCl:—Fe_2O_3, $Ba(NO_3)_2$, $MnCl_2$, As_2O_3, $CuSO_4$.

177. Name the more frequently occurring mineral compounds which are insoluble both in water and acids, and describe the processes for rendering them soluble.

178. How would you perform the qualitative analysis of an alloy containing arsenic, copper, silver, lead, and iron?

179. Name the chief blowpipe reactions employed in qualitative analysis.

PART II.

ANALYSIS OF ORGANIC SUBSTANCES.

746. All organic substances contain CARBON; a large number are composed of CARBON and HYDROGEN only; a still larger number contain OXYGEN in addition to the two last-named elements; and a large number are composed of CARBON, HYDROGEN, OXYGEN, and NITROGEN. A smaller number contain SULPHUR in addition to these four elements, and a still smaller number contain PHOSPHORUS. Organic substances, therefore, unlike inorganic ones, are all composed of some two, three, four, or five elements, and these elements are the same for all the different organic bodies. But although the formation of organic substances is restricted to some three, four, or five of the elementary bodies, their atomic constitution is far more complex than that of mineral substances, and this is one of the most marked distinctions between organic and inorganic bodies. For example, "a particle of common salt, or of cinnabar, presents a group of not more than two atoms, whilst an atom of sugar contains thirty-six elementary atoms, and the smallest particle of olive oil consists of several hundred simple atoms.

745. "It is upon the greater complexity of composition of organic bodies, together with the lesser force with which, consequently, their constituent atoms attract each other, that their easier decomposability depends: heat, for example, disturbs their composition with much greater facility than it does that

of inorganic bodies. The atoms of the former, once put in motion, or by the action of heat being separated to a greater distance from each other, arrange themselves into less complex atoms, in which the force of attraction acts in fewer directions and in which it is consequently able to oppose a proportionably stronger resistance to the further action of causes of disturbance,—decomposition."—*Liebig.*

746. Organic compounds may be analysed either with a view simply to resolve them into their *proximate constituents*, as, for instance, resolving wheat flour into its proximate constituents, starch, sugar, gluten, ligneous fibre, and oily matter; this kind of analysis is called the *proximate analysis* of organic substances; or the analysis may have for its object the mere testing the organic compound for some one or two elements, as nitrogen and sulphur; this is called *elementary or ultimate analysis.*

747. We will first describe the method of testing organic substances for nitrogen, sulphur, phosphorus, and inorganic substances,* and afterwards describe the proximate analysis of organic substances.

ELEMENTARY ANALYSIS.

748. *Test for an organic compound.*—As all organic substances contain carbon, and as very few of them contain oxygen in sufficient quantity to combine with the whole of their carbon and hydrogen, it follows that if they are heated in a closed vessel, as a small glass tube, so as to exclude the air, a black or carbonized residue will remain. No inorganic compound leaves a residue of carbon when heated under similar circumstances. Volatile bodies require to be mixed with CuO or $PbCrO_4$, and burned in a glass tube for the detection of their carbon, which is converted into CO_2, and if passed into a solution of BaH_2O_2, causes a white precipitate of $BaCO_3$, the H

---

* Animal and vegetable substances are frequently composed of inorganic as well as organic compounds, and it is as necessary to determine the nature of the inorganic as of the organic matter.

in the organic substance becomes converted into H_2O, which may be collected in drops in a cooled receiver, or passed through a tube containing $CuSO_4$, which has been dried at 205° C., water changes the colour of the dry cupric salt from white to blue.

749. *Tests for nitrogen.*—Substances containing a tolerably large quantity of N, emit in burning the familiar smell of singed hair or feathers; if this smell is distinctly perceptible, no further test is required to confirm the presence of this element. When there is no distinct smell of burnt feathers, one of the two following tests may be employed:

1st. The substance to be examined, which must be in the solid state, is mixed with solid KHO or with *soda-lime*,* the mixture is introduced into a dry test-tube, and then ignited; the C is converted into CO_2 by the O in the alkaline hydrate, while all or the greater part of the H combines with N when present, and forms NH_3, which is evolved, and may be detected in the usual way (Table 1 A 2, page 10).

2nd. "Lassaigne has proposed another method which is based upon the property of potassium to form KCN when ignited with a nitrogenous organic substance. The following is the best method of performing the experiment:—Heat the substance under examination, in a test-tube, with a small lump of K, and after its complete combustion, treat the residue with a little water (cautiously); filter the solution, add two drops of solution of $FeSO_4$ containing some ferric salt, digest the mixture a short time, and add HCl in excess. The formation of a blue or bluish-green precipitate or coloration proves the presence of nitrogen (499).

"Both methods, 1st and 2nd, are delicate; the 1st is the one most generally employed; it fully answers the purpose in nearly all cases.

3rd. "If, however, the nitrogen exists in the organic compound in an oxidized state, it cannot be detected by either of the methods just given, but it may readily be detected by heating the substance in a tube, when the evolution of red acid fumes, imparting a blue tint to iodide of starch paper, will incontestably prove it."

---

* Soda-lime is a mixture of CaO with NaHO. The lime is simply employed to prevent the soda fusing.

750. *Tests for sulphur.*—If the substance is in the solid state, it may be mixed with about twelve times its weight of pure solid KHO, and about six times its weight of pure KNO_3; or it may be intimately mixed with some pure KNO_3 and Na_2CO_3; the mixture is then heated to fusion in a crucible. The fused mass is allowed to cool, then dissolved in water, the solution acidified with HCl and tested subsequently for H_2SO_4 with $BaCl_2$.

751. Fluids are treated with fuming HNO_3, or with a mixture of HCl and $KClO_3$, at first in the cold, finally with heat; the solution is then tested for H_2SO_4 with $BaCl_2$ or $Ba(NO_3)_2$

752. As the two methods just described serve simply to indicate the presence of sulphur in a general way, but afford no information regarding the state or form in which that element may be present, we give another method (753), which serves to detect only the sulphur in the non-oxidized state in organic compounds.

753. Boil the substance with a strong solution of KHO, and evaporate nearly to dryness. Dissolve the residue in a little water, pour the solution into a flask,* and slowly add dilute H_2SO_4 through the funnel-tube, if sulphur is present the *lead test-paper* will turn brown.

754. *Tests for phosphorus.*—The methods described in pars. 750 and 751, will likewise serve for P. The solutions obtained are tested for phosphoric acid either according to par. 424, 427, or 428. If the method described in par. 751 has been employed the greater part of the HNO_3 must be removed before employing the test. The P may be detected by slightly

---

* The flask must be provided with a funnel-tube which is fitted into a cork, on the under surface of the cork is attached a slip of paper which has been thoroughly moistened with a solution of lead acetate, and then touched with a few drops of a solution of $(NH_4)_2CO_3$.

carbonizing the substance, then reducing it to powder, and conducting the operation as at par. 431.

755. *Test for inorganic substances.*—"A portion of the substance under examination is heated on platinum foil, to see whether or not a residue remains. When acting upon difficultly combustible substances, the process may be accelerated by heating the spot which the substance under examination occupies on the platinum foil, to the most intense redness, directing the flame of the blowpipe upon the corresponding point of the lower surface of the foil." The methods for examining the residue are described in pars. 760 to 771.

PROXIMATE ANALYSIS OF ORGANIC SUBSTANCES.

756. Organic substances, like inorganic ones, are either acids, bases, salts, or indifferent bodies; and the resolution of organic componnds into their proximate constituents, is effected by methods perfectly similar to those used in the analysis of inorganic compounds; that is, the operator endeavours to separate (by solvents, application of heat, &c., &c.) the individual constituents from one another, either in the *direct* way, or after having previously converted them into appropriate forms.

757. Of the solvents employed in organic analysis ether is particularly valuable as a solvent for fatty substances, and for caoutchouc and camphor; alcohol, for the solution of many crystallizable organic principles, such as the vegetable alkalies; whilst water dissolves sugar, gum, starch, and other bodies, which are nearly insoluble in alcohol and ether. In some cases benzole, in others chloroform, is a valuable solvent, and may be substituted for ether, which they most resemble in their solvent action. In particular cases dilute acids, and in others dilute alkalies may be employed, but they must be used with caution, as they are liable to act not merely as solvents, but also to produce important chemical changes upon the compounds submitted to them. No general rule can be laid down for the extraction of the different proximate principles, each class

of substances requiring special modifications, which experience alone can indicate.

758. In all cases of proximate analysis, the employment of the microscope will be found invaluable as a means of watching the progress of the separation of the various principles, and of ascertaining whether the substances which the chemist has isolated are mixed with other bodies which may resemble them in chemical habitudes. When a substance or deposit assumes the crystalline state, such an examination, by revealing the similarity or difference in form of its component particles, is often more valuable for ascertaining the purity of a substance than ordinary chemical reagents.—*Miller.*

759. We shall now give the method for the examination of the ash, whether derived from animal or vegetable substances, and we shall then give under Animal and Vegetable Chemistry' the properties and reactions of the chief organic compounds of animal and vegetable origin, and along with this the proximate analysis of mixed animal substances and the analysis of urine.

EXAMINATION OF THE INORGANIC CONSTITUENTS OF ANIMAL AND VEGETABLE SUBSTANCES.

760. *Preparation of the ash.*—The incineration of the substance* is best effected by placing it in a platinum dish, or other shallow vessel, and introducing the vessel into a muffle, which should then be gradually heated; but not carried beyond a very faint redness.† For merely qualitative analysis it will generally be found sufficient to char the substance in a porcelain or platinum dish, with the aid of a wide glass tube or lamp-glass to increase the draught. "The heat must always be moderate to guard against the volatilization of certain constituents, more especially of metallic chlorides. It is not

---

* Before incinerating the substance care must be taken to free it from all adhering impurities, as these are frequently attached to plants.

† Substances to which this mode of incineration is unsuited, are charred first at a gentle red heat in a large covered platinum or Hessian crucible, and the charred mass is subsequently incinerated in the muffle.

always necessary to continue the combustion until all the carbon is consumed. With ashes containing a large proportion of fusible salts, as *e. g.* the ash of beetroot molasses, it is even advisable at first, simply to char the mass in a crucible at the lowest possible temperature, then to treat with water until the principal portion of the soluble salts is extracted, afterwards dry the residue, and finally, incinerate it in the muffle" (*Fresenius*). Alkaline sulphates are frequently converted by the reducing action of carbon, into sulphides and hyposulphites. The ashes of animal substances often contain cyanates, which are best destroyed by moistening the ashes with water, and then gradually heating to redness; one moistening is usually sufficient to convert them completely into carbonates.

761. *Analysis of the ash.*—In the qualitative examination it is usual to examine the aqueous solution, the HCl solution, and the portion insoluble in acids separately—supposing the ash is not entirely soluble in water—as we thereby obtain a better acquaintance with its general character, and in the state or condition in which the constituents are present. In this examination we shall confine ourselves to the natural constituents of the ashes of plants and animals; if accidental constituents require to be sought for, a complete qualitative inorganic analysis, according to the methods given in Part I of this work, must be undertaken.

762. The following are the natural constituents:—

Bases.	*Acids.*
Iron oxide.	Silica.
Manganese oxide.	Phosphoric acid.
Lime.	Sulphuric acid.
Magnesia.	Carbonic acid.
Soda.	Chlorine.
Potash.	Fluorine.
Lithia.*	Iodine.†

---

* Lithia has lately been found in the ash of many plants; Rubidium has also been found, but this can only be discovered by spectrum analysis.

† Iodine and bromine need only be looked for in marine plants.

763. Boil the ash with water, filter, and examine the filtrate according to next par., and the portion insoluble in water after it has been well washed according to par. 767.

764. *Examination of the aqueous solution.*—Add to about one-half the aqueous solution HCl, if effervescence ensues, it may be due to CO_2, H_2S, or SO_2, arising from the decomposition of hyposulphites; examine the evolved gas for carbonic acid according to par. 441; the other two gaseous acids need not be attended to, as they, if present, are only due to the reduction of the alkaline sulphates (406).

765. Evaporate the solution, which has been acidulated with HCl, to dryness, treat the residue with HCl and water; if a portion remains undissolved it is due to silicic acid, in this case filter and add to the filtrate, or to the solution if there is no silicic acid, NH_4HO slightly in excess, and then acetic acid in excess, and then a drop of Fe_2Cl_6 (427); if a precipitate is produced, phosphoric acid is present, in that case add more Fe_2Cl_6 until the solution is of a slightly reddish colour. Boil the solution whether phosphoric acid is present or not, in order to get rid of the iron which has been added; when all the iron has been precipitated, which is known by the complete decoloration of the liquid, filter, and to the filtrate add NH_4HO and $(NH_4)_2C_2O_4$, if, after allowing the liquid to stand for some three or four hours a precipitate is formed Ca is present;* filter and divide the filtrate into two parts, to one part add NH_4HO and Na_2HPO_4, if a precipitate is formed after some time, Mg is present. Evaporate the other portion of the filtrate to dryness, and ignite to get rid of and burn off all carbonaceous matter; examine the residue for Na (51), for K (46), and for lithia (61).

766. Add to a portion of the aqueous solution, which has not been acidified, $AgNO_3$ as long as a precipitate continues to form; warm gently, and then cautiously add NH_4HO; if a

---

* If CO_2 is present, Ca and Mg must of course be absent, when this is the case, divide the filtrate from the silicic acid precipitate into two portions, test one for phosphoric acid by adding NH_4Cl, NH_4HO, $MgSO_4$ (424), and test in the other portion for Na, K, and Li, in the manner directed in pars. (51, 46, 61).

black residue is left, this consists of Ag_2S, proceeding from a sulphide or a hyposulphite. Mix the ammonic solution—after previous filtration if necessary—cautiously with *pure* HNO_3 in slight excess, to effect the solution of the precipitate of silver phosphate formed, thus leaving only AgCl, AgI, AgBr undissolved. Test separately for I according to 540, for Br 541, for Cl 539. Neutralize the filtrate from the portion of the Ag precipitate insoluble in HNO_3 exactly with NH_4HO; if on the neutralization, a *bright yellow* precipitate is produced, it is ortho-phosphoric acid that is present, but if the precipitate is *white*, the acid is either the pyrophosphate or the metaphosphate.*

---

* If a phosphate contains three atoms of fixed base, the fluid, after the complete precipitation of the phosphoric acid by means of $AgNO_3$, will be neutral, but if it contained only two atoms or one atom of fixed base, the fluid after the precipitation of the acid with the silver salt, will be acid. Further, argentic ortho-phosphate (Ag_3PO_3) is yellow, whilst argentic pyro-phosphate ($Ag_4P_2O_7$), and meta-phosphate ($AgPO_3$), are white. Again, an ortho-phosphate containing two atoms of fixed base is converted by ignition into a pyro-phosphate; and an ortho-phosphate containing one atom of fixed base is converted by ignition into a meta-phosphate. We will now see how Liebig employed these facts in his investigation into the constitution of the ash of the juice of the flesh from different animals:

Liebig found that the ash of the juice of the flesh in the case of the ox, horse, fox, and roe-deer, gave with water a strongly alkaline solution, and that it was precipitated, first white, then yellow, by neutral $AgNO_3$; and the mixture, after complete precipitation, was perfectly neutral. This proves that the ash contains an alkaline pyro-phosphate and an alkaline ortho-phosphate. When this ash was mixed with HNO_3, dried up, and again ignited (by which means the Cl of the alkaline chlorides was expelled), and the metals added to the phosphates in the form of oxides, the proportion between the *white* and the *yellow* precipitate with $AgNO_3$ was altered, the quantity of the yellow precipitate being increased; but the two colours of the precipitate were constantly observed.

The ash of the juice of the flesh of fowl, Liebig discovered, gave a different result. The aqueous solution gave with $AgNO_3$ a precipitate of *pure white*; the ash, therefore, contains an alkaline pyro-phosphate, and when it was acted on by HNO_3 and again ignited, the soluble portion still precipitated $AgNO_3$ *only* white, although an additional quantity of alkali was thus added to the phosphate originally present. From this it follows, that the juice of the flesh of fowl must contain a certain, though small quantity

767. Warm then the portion of the ash insoluble in water, with HCl, if effervescence ensues it indicates CO_2 combined with Ca or Mg; if Cl is evolved it denotes one of the higher manganese oxides.

768. *Examination of the hydrochloric solution.*—Add NH_4HO very slightly in excess, then add acetic acid in excess; if a white precipitate remains undissolved by the acetic acid it is due to the presence of ferric phosphate; filter a small portion of the liquid, and test for Fe''' with K_4FeCy_6, if it is present in the filtrate it shows that all the iron does not exist as phosphate; if there is no iron present in the filtrate add some Fe_2Cl_6 to the unfiltered portion until the fluid looks reddish; in either case, that is, whether the iron is in excess or it is added in excess, boil the unfiltered portion until it is all removed; when this is accomplished filter hot, and add to the filtrate NH_4HO and $(NH_4)_2S$, and allow it to stand in a corked flask for some time; if a precipitate should form, test it for Mn; filter and examine the filtrate for Ca and Mg in the usual way.

769. *Examination of the residue insoluble in hydrochloric acid.*—The residue insoluble in HCl contains—

1. The silicic acid which has separated on treating with HCl.

2. Those ingredients of the ash which are insoluble in HCl. These are, in most cases, ashes, sand, clay, carbon; substances, therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. Only the ashes of the stalk of cereals and others abounding in silicic acid are not completely decomposed by HCl.

770. It is rarely necessary in an examination which is not going to be extended beyond a qualitative analysis to examine this residue further; but in cases where it is desirable, the

---

of an alkaline metaphosphate, since, otherwise, after the action of HNO_3 on the ash, a certain quantity of an alkaline ortho-phosphate must have been produced, and thereby a yellow precipitate must have been formed, to a corresponding extent, with $AgNO_3$.

analysis for all the bases, with the exception of the alkalies, must be conducted according to par. 725, and for the alkalies according to par. 729.

ANIMAL CHEMISTRY.

771. We shall first give in groups, as far as it is possible, the chief organic compounds met with in the animal organism, with their properties and reactions; and afterwards a method for the proximate analysis of mixed animal substances (940), and lastly a method for the analysis of urine (964). Before commencing the proximate analysis the student is recommended to go through the chief groups, performing all the experiments given.

THE ALBUMINOID OR PROTEIC GROUP.

ALBUMEN, FIBRIN, CASEIN, GLOBULIN, VITELLIN.

772. *Properties of the Group.*[*]—The members composing this group are met with in the vegetable as well as the animal kingdom; they are uncrystallizable, and in their pure state they are tasteless and inodorous. They exist in the living organism both in the soluble and insoluble state; they are present in the soluble form in the fluids, and in the insoluble form in the solid parts of plants and animals. When freshly precipitated from their solutions, and whilst still moist, they are usually whitish in colour, and appear as a flocculent precipitate or in small clots; when dried and unpowdered they are tough and gelatinous.

773. These substances when dried, and if not exposed to moist air, will keep for any length of time unchanged. But if

---

[*] Globulin is not included in the remarks on the properties of the group; these observations only strictly apply to albumen, fibrin, and casein.

moist, or exposed to moisture, they speedily decompose and putrefy, and this is one of their most striking characters; they are *ferments* in their decomposing or putrefying state, yeast, wine-lees, diastase, synaptase, pepsin, for instance, are albuminoids in a peculiar state of decomposition.

774. If these bodies are heated in close vessels (subjected to dry distillation), they first swell up and fuse, then blacken, and emit a large quantity of fœtid empyreumatic products, among which NH_3 and H_2S are always present; and they leave in the retort a porous, brilliant, carbonaceous mass. When burned they leave a notable amount of ash; this varies in quantity in different cases, but it always contains phosphate of lime.

775. They all yield the same products when treated with oxidizing agents, such as MnO_2, or $K_2Cr_2O_7$ and H_2SO_4; the volatile products are the only class which have been fully examined, the following are the volatile substances which have been identified:

Formic acid.
Acetic acid.
Propionic acid.
Butyric acid.
Valeric acid.
Caproic acid.
Acetic aldehyd.
Propionic aldehyd.
Butyric aldehyd.
Benzoic acid.
Hydride of benzoyl.
Hydrocyanic acid.
Valeronitrile.

776. The albuminoids are insoluble in alcohol and ether, and are even precipitated from their aqueous solutions on the addition of alcohol to the liquid; the precipitate is generally insoluble in water after its precipitation by alcohol.

777. "These substances either in their soluble, or insoluble state, are readily dissolved by the aid of a gentle heat in a solution of KHO or NaHO, the addition of an acid to their alkaline solution so obtained causes the separation of a greyish flocculent precipitate, termed by Mulder protein, while a slight odour of H_2S is emitted, and a small quantity of phosphoric

acid is also found in the solution. This precipitation is best effected by means of acetic acid, since the mineral acids are obstinately retained by the flocculi."—*Miller*.

778. In concentrated H_2SO_4 these substances dissolve with a brownish-red colour.

779. Concentrated HNO_3 produces in solutions of these substances a precipitate of a bright orange colour, which gradually dissolves in the acid with effervescence; HNO_3 added to the substances in the insoluble state colours them yellow and finally dissolves them. Mulder considers the yellow colour to be due to the formation of a distinct compound which he has called *xanthoproteic* acid.

780. When to a solution of these substances concentrated HCl is added, and the solution is gently warmed, a white precipitate is first produced, which gradually dissolves, forming, if in contact with atmospheric air, a blue or violet-coloured liquid. The reactions with HNO_3 and HCl are very characteristic of the albuminoids.

781. Most acids produce a precipitate in solutions of these substances, but when they are added in excess redissolve the precipitate; when these acid solutions are diluted with a moderate quantity of water, a precipitate is formed which disappears on the further addition of water.

782. Metaphosphoric acid produces a precipitate in solutions of these substances, but an excess of the acid does not redissolve the precipitate.

783. Tannic acid produces a precipitate in solutions of these substances, and an excess of the acid does not redissolve the precipitate.

784. The acid solutions, but not the aqueous solutions, of the albuminoids give a precipitate with potassic ferrocyanide and ferricyanide; the next group of substances gives no precipitate with these reagents.

785. If a solution of Hg, prepared by dissolving two parts of it in four parts of HNO_3, of sp. gr. 1·40, be added to a solution of the albuminoids, or, if in the solid state, they are moistened with the Hg solutions, and the moistened solid or

the fluid is then heated to a temperature from 60° to 100° C., an intense red colour is produced, which is not destroyed by boiling water, nor by exposure to the air; the colour is so intense that it may be perceived on adding the mercurial solution to a liquid containing not more than 1 part of albumen in 100,000 parts of water. The Hg solution gives a similar coloration with the members of the next group.

786. The aqueous solution of these bodies is precipitated by copper, lead, and mercury salts, the precipitate generally consists of the employed salt as well as the albuminoid.

787. If a solution of these substances be mixed with a solution of $CuSO_4$, and then a large excess of KHO be added, the greenish precipitate first formed is redissolved, and the liquid acquires a purple tint of great intensity and magnificence. The same reaction takes place with the next group of substances, and probably with any of the more complex nitrogenous substances.

788. In the living organism, fibrin, casein, and albumen are converted into one another, for example, the casein in milk, when this substance is used as food, must be converted in the animal economy into albumen and fibrin, and the two latter albuminoids must be converted into casein in the formation of milk. As the albuminoids have the same or nearly the same constitution, as shown by the following analyses, their conversion into one another can be easily accounted for. In the subjoined analyses the ash has been deducted previous to calculating the composition in 100 parts:—

	Albumen.	Fibrin.	Casein.
Carbon	53·3	53·0	53·83
Hydrogen	7·2	6·9	7·15
Oxygen	22·	23·5	22·52
Nitrogen	15.7	15.4	15·65
Sulphur	1·8	1·2	0·85
	100.0	100·0	100·00

789. The determination of the *rational formula* of bodies

like the albuminoids is beset with difficulties; the difficulties are so great with regard to these substances that they have not yet been overcome, and consequently their rational formula has not been determined. Different views have, however, been put forward to explain the relation between them, for, from their great similarity in composition and properties, there can be no doubt but that they are very closely related. The first view we shall notice is that of Mulder, as, although now abandoned, it is constantly referred to in works on the science; this view when first promulgated by the author was almost universally accepted by chemists, but they have long regarded it as erroneous.

790. Mulder considered that the flocculent precipitate obtained by adding an acid to an alkaline solution of the albuminoids was free from sulphur and phosphorus, and that this nitrogenized precipitate has identically the same composition, whether obtained from fibrin, albumen, or casein. This substance, which he called protein, he regarded as the fundamental principle of each of the albuminoids, and that albumen, fibrin, and casein were produced by the combination of different quantities of sulphur and phosphorus with protein; admitting this view of the construction of these bodies, it was easy to account for their conversion into one another, for the elimination or combination of small quantities of sulphur and phosphorus was all that was required to effect the change.

791. The so-called protein substance, Liebig has shown, is never obtained free from sulphur, that it always contains a small but variable quantity of this element; he considers that the precipitate is not a new and distinct substance, but that it is the original body slightly modified by the action of the potash.

792. " Gerhardt was of opinion that all the albuminoids are identical, not only in composition, but in chemical constitution, and that they differ from one another only in molecular arrangement, and by the nature of the mineral substances with which they are associated; in fact, that they contain a common proximate element, which, like many other organic compounds, is capable of existing in a soluble and an insoluble modification.

Designating this common element by the name albumin, he supposed that white of egg and serum consist of acid albuminate of sodium, which is separated by heat into free albumin and neutral albuminate of sodium, the latter remaining dissolved; that casein, which is soluble and non-coagulated by heat, consists of neutral albuminate of potassium, from which the organic compound may be precipitated by neutralizing the alkali with an acid; and that fibrin is albumin in the insoluble state, more or less mixed with earthy phosphates. This view is in accordance with the fact that fibrin and casein may be dissolved in neutral potash salts (better with addition of a little caustic alkali), forming a liquid which coagulates by heat, and deflects the plane of polarization of a luminous ray to the left, like albumin; and that fibrin and albumin, dissolved in a certain quantity of caustic alkali, exhibit the characters of soluble casein. Nevertheless, it is possible to obtain the albuminoids in some cases wholly, in others very nearly, free from mineral matters, and nevertheless exhibiting their distinguishing characteristics.

793. "Strecker supposes the albuminoids to be composed of a great number of radicles (a supposition in accordance with the variety of their products of decomposition), that the greater number of these radicles are the same in all, hence their great similarity; but that each contains one or more such radicles peculiar to itself. Thus, when casein is converted in the animal body into albumen and fibrin, it may take the radicles required for that transformation from the other constituents of the milk, viz. the fat and the sugar."—*Watts' 'Dictionary of Chemistry.'*

ALBUMEN.

794. *Properties of soluble Albumen.*—An aqueous solution of albumen is a tasteless, odourless, and colourless, but somewhat glairy, liquid. It exerts a left-handed rotatory action upon a ray of polarized light. It is adhesive, and when spread

on paper it forms when dried a varnished surface. Soluble albumen in the solid state is translucent and of a pale yellow colour; it is tasteless and odourless; it swells in water, assuming a gelatinous appearance: it does not dissolve freely in pure water, but very readily in water containing any alkaline salt.

795. If its aqueous solutions are evaporated to dryness at a temperature *not exceeding* 49° C., the solid albumen thus obtained will dissolve, although slowly, in water; its solution is greatly promoted by the addition of NaCl or any salt of the alkalies; a varying quantity of the albumen always becomes converted by the evaporation into the insoluble state.

796. If an aqueous solution of albumen is heated to about 66° C. it becomes opalescent, and at 77° C. it becomes entirely converted into the insoluble form. This conversion of the soluble into the insoluble form by heat, is the most characteristic property of albumen. The reason of the conversion is not known. Dumas thinks that it is probably a simple isomeric modification analogous to the conversion of cyanic into cyanuric acid.

797. *Action of alcohol, ether, &c. on soluble Albumen.—Strong* alcohol precipitates albumen from its solutions, and after its precipitation by this liquid it will not redissolve in water. If the alcohol is rendered slightly alkaline by KHO it causes no precipitate in solutions of albumen. *Weak* alcohol also precipitates albumen from its solution, but the precipitate redissolves completely in water.

798. *Ether*, if free from alcohol, only gelatinizes the albumen, it does not coagulate it.

799. *Kreasote* and *aniline* precipitate and coagulate it immediately.

800. *Rennet* does not precipitate it from its solutions. The *volatile* and *fixed* oils have no action upon it.

801. *Action of acids on soluble Albumen.*—The action of concentrated H_2SO_4, HCl and HNO_3 on albumen, and the other albuminoids has already been noticed (778, 779, 780).

802. Dilute H_2SO_4 produces no precipitate in solutions of albumen until the liquid is boiled.

803. Dilute HCl precipitates it at first, but afterwards redissolves it; this solution becomes milky on the addition of a little water; but if more water is added it becomes perfectly clear again.

804. Dilute HNO_3 precipitates it readily and completely, and does not redissolve it; the precipitate is soluble in a large quantity of water. Dilute HNO_3 is frequently employed as a test for the presence of albumen.

805. Metaphosphoric acid precipitates it immediately and completely. The ortho- and pyro-phosphoric acids do not precipitate it.

806. The organic acids, tannic acid excepted (783), cause no precipitate in moderately concentrated solutions of albumen: its solutions, in the presence of organic acids do not coagulate by heat, but a pellicle gradually forms over the surface during evaporation.

807. Serum or white of egg mixed with a certain quantity of NaCl, or other salt of an alkali-metal, forms a liquid precipitable by phosphoric, acetic, tartaric, oxalic, and lactic acids, &c.; conversely, a solution of albumen (or other albuminoidal substance) in acetic acid is precipitated by the salts of the alkali-metals. The precipitation is greatly facilitated by heat, and likewise takes place with greater facility as the proportion of salt added is greater. The precipitate dissolves in pure water, with greater facility in proportion as less heat has been applied in producing it; the solution is not coagulated by heat. It is soluble also in acetic acid, phosphoric acid, and even in alcohol, provided it has not been altered by desiccation, or by contact with the air. The aqueous solution is precipitated by certain salts, potassic ferrocyanide for example.

808. When a small quantity of acetic acid is added to white of egg or serum, so as just to saturate the alkali, and the liquid is then largely diluted with water, flocks of albumen are deposited after a while. If the supernatant liquid be then decanted, and the precipitate treated with a small quantity of solution of

KNO_3 or NaCl, it immediately dissolves, and the solution is coagulated on boiling.

809. *Dried soluble* albumen suspended in acetic, tartaric, or citric acid, swells up and is converted into coagulated albumen, which may be completely freed from acid by washing.

810. Cl and Br precipitate albumen from its solutions.

811. *Action of salts on soluble Albumen.*—"The greater number of the metallic salts, as iron, copper, lead, mercury, silver, antimony, aluminum, precipitate albumen; the precipitate consisting either of a combination of a basic salt with albumen, or a mixture of two compounds, one of which consists of the acid of the salt and albumen, and the other of the base of the salt and albumen. The albumen generally passes into the insoluble state in these combinations; the precipitate is generally soluble in an excess of serum or white of egg, and in some cases in the salt which produces it. Albumen, owing to its forming precipitates with them, is a valuable antidote in cases of poisoning by metallic salts.

812. "$HgCl_2$ is a delicate test of the presence of albumen, a liquid containing only a two-thousandth part of solid albumen is precipitated by it. The white precipitate formed is an insoluble compound of the salt with the organic substance; albumen, it is well known, is the antidote which is employed in this form of poisoning."

813. *The action of the alkalies and alkaline carbonates on soluble Albumen.*—The presence of an alkali, or an alkaline carbonate, in a liquid containing albumen, greatly modifies the reactions of that substance; if the alkali is present in considerable quantities the solution does not coagulate by heat; but if it be evaporated, a pellicle forms over the surface similar in appearance to that produced upon a solution of casein by heat. Also, if to an alkaline solution of albumen, acetic, tartaric, or ortho-phosphoric acid, acids which in neutral or slightly alkaline solutions of albumen cause no precipitate, is added, a precipitate is produced which readily dissolves in an excess of the acid. These characters resemble those of casein and some

chemists have supposed that casein is simply an albuminate of potash.

814. If alcohol be added to an alkaline solution of albumen, it causes, as we have already noticed, no precipitate.

815. If a concentrated solution of KHO be added to a concentrated solution of albumen, albuminate of potash in the form of a gelatinous mass is produced; by washing the precipitate with cold water the greater part of the alkali can be removed, 5·4 per cent. of the alkali only remaining. If the gelatinous mass be washed with alcohol and then with water, it is insoluble in boiling alcohol and boiling water; but if it be washed with cold water, it is soluble in boiling water and boiling alcohol.

816. *Properties of insoluble Albumen.*—Insoluble albumen when moist appears as a white opaque elastic solid, it turns blue litmus *red.* When dried it is of a pale yellow colour, and becomes brittle and translucent like horn. If the dried substance be immersed in water it absorbs about four or five times its weight of water and regains the consistence of the undried substance. When coagulated albumen is boiled in water for about sixty hours in open vessels it undergoes gradual decomposition, and a soluble compound is obtained which according to Mulder is teroxide of protein and ammonia. If heated to 149° C. with a small quantity of water in a sealed tube the albumen is redissolved, and furnishes a liquid which does not coagulate by heat, but which, when acidulated with acetic acid, gives a precipitate with potassic ferrocyanide.

817. *On the varieties of Albumen.*—"The properties of albumen vary in some degree with the source from which it is derived. The differences may in some cases be attributed to the presence of different mineral substances, but in others they are of such a nature as rather to point to the existence of different modifications of albumen. Thus Frémy and Valenciennes have found that the albumen of the eggs of certain tribes of birds exhibits peculiar modifications. That from the eggs of different species of gallinaceous birds always exhibits the characters above described; but the eggs of swimming

and wading birds yield an albumen which, when diluted with three measures of water, is not coagulated by heat, but is precipitated by HNO_3; and the albumen from the eggs of predacious birds and some kinds of perching and climbing birds is neither coagulated by heat nor precipitated by nitric acid. The composition was, however, found to be the same in all cases.

818. "Blood-albumen exhibits the same reactions as that from white of egg, excepting that the latter when boiled gives up part of its sulphur in the form of sulphuretted hydrogen, which blood-albumen does not; nevertheless coagulated white of egg appears to contain more sulphur than blood-albumen.

819. "Scherer found in a liquid obtained from a case of ovarian dropsy a substance resembling albumin, but differing from it in not being completely precipitated by ebullition even after addition of acetic acid, and in dissolving in water after being precipitated by alcohol; this modification he named *Paralbumin.*

820. *Metalbumin* is the name given by the same chemist to another supposed modification of albumin, likewise obtained from a pathological fluid, which exhibited similar peculiarities to the preceding, and was further distinguished by giving no precipitate with HCl, or with potassic ferrocyanide after acidulation with acetic acid."—*Watts' Dictionary of Chemistry.*"

FIBRIN.

821. Fibrin exists only in solution in the living plant or animal, for as soon as the solution is removed from the living organism it immediately begins to coagulate; this character distinguishes it from other analogous substances. The coagulation of the fibrin is prevented if the blood or other liquid containing the fibrin, at the moment it leaves the living organism, is mixed with solutions of certain salts, such as potassic carbonate or nitrate, sodic acetate, sulphate or chloride.

822. *Properties of Fibrin.*—Undried coagulated fibrin ap-

pears in the form of long, white, elastic filaments, but when dried it forms a horny yellowish or grey solid. Both in the dried and undried state it is tasteless and insoluble both in hot and cold water, in alcohol, ether, &c. When long boiled, however, with water, it is, like albumen, gradually dissolved; by the exposure to heat and moisture it has evidently undergone decomposition, for the solution contains traces of ammonia. If undried fibrin is covered with water, it becomes in a few days viscid and acquires the odour of old cheese.

823. *Action of acids on Fibrin.*—The action of concentrated HCl, H_2SO_4, and HNO_3, on fibrin and the other albuminoids has already been noticed (778, 779, 780).

824. When fibrin is immersed for about twelve hours in water slightly acidulated with HCl, it becomes gelatinous, and when this jelly is triturated with water, it yields a solution which coagulates by heat, is precipitated by potassic ferrocyanide, and affords a precipitate on the addition of HCl, not soluble except in an excess of this acid. According to Dumas and Cahours, water containing a millionth part of HCl or HBr gelatinizes fibrin, and if a few drops of gastric juice (pepsine) be then added, it is entirely dissolved in a couple of hours at a temperature of 35° to 38° C. Rennet produces the same effect.

825. Metaphosphoric acid does not dissolve fibrin. Orthophosphoric acid converts it into a gelatinous mass which is soluble in water, the fibrin is not precipitated from this solution on the further addition of the acid.

826. Concentrated acetic acid converts it into a gelatinous mass which is soluble in pure water. H_2SO_4 and HPO_3 precipitate it from this solution, the precipitate consisting of a compound of fibrin and the precipitating acid. Potassic ferrocyanide precipitates fibrin from its acetic solution. Alkalies also precipitate it, but it is redissolved by an excess of the alkali. According to Dumas the fibrin of young animals is more easily acted on by acetic acid than that of old ones, so that there is in this respect a material difference between the fibrin of veal and of beef.

827. *Action of the alkalies on Fibrin.*—Weak solutions of KHO and NaHO dissolve fibrin, NH_4HO exerts the same influence, but less rapidly; acetic and phosphoric acids and also the metallic salts precipitate fibrin, as they do albumen, from its alkaline solutions. Indeed an alkaline solution of fibrin resembles an alkaline solution of albumen in most of its characters.

CASEIN.

828. *Properties of soluble Casein.*—Although this substance is met with in a state of solution in milk it is doubtful whether it has a soluble form; it is considered that its soluble state in milk is due to a small quantity of free alkali; casein in solution does not coagulate by heat, the solution merely becomes covered with a film which is formed as often as it is removed. The casein of milk when obtained in the solid state does not redissolve completely in water.

829. *Action of alcohol, rennet, &c., on soluble Casein.*—Casein in solution is coagulated by alcohol, a portion at the same time entering into solution; a larger quantity is dissolved by boiling alcohol. The coagulum produced by absolute alcohol is insoluble in pure water; but the portion dissolved by alcohol is, after the removal of the alcohol, found to be still soluble in water.

830. Rennet (the inner membrane of the fourth stomach of the calf, salted and dried), or an infusion of it prepared at a low temperature, coagulates casein completely; this is the most remarkable and important mode of coagulating casein.

831. *Action of acids on Casein.*—The action of concentrated HCl, H_2SO_4, and HNO_3, on fibrin and the other albuminoids has already been noticed (778, 779, 780).

832. Casein is precipitated from its solutions by all acids with the exception of carbonic acid, the precipitate redissolves in an excess of the acid; from its solution in acetic acid the mineral acids and potassic ferrocyanide precipitate it.

833. The coagulation of milk is due to the lactic acid, which is formed from lactine, neutralizing the alkali which renders the casein soluble, and thus causing that substance to pass into its insoluble state.

834. *Action of bases and of salts.*—" Coagulated casein is readily dissolved by solutions of the alkalies and of the alkaline carbonates; and if the solution be very feebly alkaline, the alkaline reaction may be completely neutralized by the casein. Solutions of NaCl, of KNO_3, and of NH_4Cl, likewise dissolve casein with facility, and these solutions, when evaporated by the aid of heat, become covered with an insoluble pellicle. Casein also unites with the alkaline earths and forms compounds which are insoluble in water. If a piece of poor cheese, which consists principally of casein, be reduced to a paste with water and mixed with CaH_2O_2, it produces a tenacious lute, which sets very hard, and may be used for cementing pieces of broken earthenware. In consequence of the tendency to the formation of these insoluble compounds, a solution of casein is precipitated by calcic salts or by $MgSO_4$, upon the application of heat to the mixture; this reaction is very characteristic of casein. Most of the metallic salts, such for instance as acetate and basic acetate of lead, $CuSO_4$, $HgNO_3$, and $HgCl_2$, occasion precipitates in the cold with solutions of casein."—*Miller.*

GLOBULIN.

835. Globulin occurs in the cells of the crystalline lens in a very concentrated solution; it was also considered to be present in red globules of Vertebrata, but later researches regard the two substances as distinct, the substance extracted from the blood is called Hæmatoglobulin or Hæmatocrystallin; it is decomposed by heat, by alcohol, by acids, and by alkalies into hæmatin and albumen.

836. Globulin is very similar to albumen in its properties, but it is distinguished from that substance by " its solutions not becoming opalescent at a lower temperature than 73°; at

83° it assumes a milky turbidity, and at 93° C. separates as a milky coagulum which never becomes clear on filtration, and from which neither small quantities of acetic acid nor ammonia separate flakes capable of being removed by filtration; it is only when neutral alkaline salts are added, and the solution is then boiled, that the fluid becomes perfectly clear and flakes and small clots are deposited. The following reaction is very characteristic of globulin; its solution is not precipitated either by acetic acid or by ammonia, but it becomes strongly turbid when the fluid treated with acetic acid is neutralized with ammonia, or conversely when after the addition of ammonia it is neutralized with acetic acid. No other *soluble* albuminoid is precipitated both from its acid and its alkaline solution by neutralization, although almost all the *insoluble* albuminoids possess this property—a circumstance which affords a proof that globulin is reduced to the coagulated state both by an excess of alkali and by an excess of acid."—*Lehmann.*

837. *Vitellin.*—This name was given to the albuminous body of the yelk of egg; it is now known to be merely a mixture of albumin and casein.

838. *Recapitulation and remarks.*—This group of substances is distinguished from a large number of substances by *containing nitrogen;* the method for testing organic substances for this element is given at par. 749.

839. The substances forming this group are distinguished from a large number of organic substances containing nitrogen, by containing sulphur; the method for testing organic substances for this element is given at pars. 750 to 754. They are distinguished from the next group of substances by being precipitated from their acid solutions by potassic ferrocyanide.

840. Albumen is usually distinguished and separated from the other members of the group, by warming the fluid and coagulating; if the solution is alkaline it is necessary to *neutralize* it with acetic acid, care being taken not to add the acid in excess before warming the liquid; if the solution is very acid it ought to be neutralized, or the acid or alkaline liquid, instead of being neutralized, is treated with a strong saturated solu-

tion of NH_4Cl; when NH_4Cl is employed, the solution requires a longer boiling in order to completely precipitate the albumen from the fluid than if it had been neutralized.

841. Fibrin is distinguished from the other albuminoids by the property which it possesses of coagulating spontaneously; it can exist only in the soluble form in the living plant or animal.

842. Casein in the absence of, or after the removal of, albumen, may be detected by adding to the solution $MgSO_4$, or $CaCl_2$, and then warming the solution; if casein is present a precipitate will be formed. But the test which distinguishes it from the other albuminoids is rennet; to render this test reliable, the rennet must be tolerably fresh, or at least free from all putridity; the mixture should be digested for a period not exceeding two hours, and at the temperature of 40°C.

GELATIGENOUS GROUP.

GELATIN. CHONDRIN.*

843. *Properties of the group.*—Under the term gelatin we include the organic tissue of bone, cartilage, sinew, ligament, skin, cellular tissue, and serous membrane; all these substances dissolve by long-continued boiling in water, and the solution on cooling becomes a consistent gelatinous mass. It is represented in various degrees of purity by glue, size, and isinglass. Gelatin does not exist *as gelatin* in the animal tissues, but is formed from them by the action of boiling water. Müller has shown that there are two (if not three) distinct forms of gelatin. To that which is obtained from the permanent cartilages, the cornea, fungous bones, &c., the term *chondrin* is given, while *glutin* includes those forms of gelatin which are obtained from skin, serous membrane, hoof, bone, tendon, fibrous and spongy cartilage, cartilage of bone, &c.

---

* There are two other bodies known—Fibroin and Chitin—which belong to this group, but we have omitted them on account of their unimportance.

844. The gelatigenous substances have hitherto been found only in animals. They contain a smaller amount of carbon and sulphur and a larger amount of nitrogen than the members of the albuminoid group, as will be seen on comparing the following table with the one given at par. 788.

	Chondrin.	Gelatin.
Carbon	49·97	50·40
Hydrogen	6·63	6·64
Nitrogen	14·44	18·34
Sulphur	0·38	24·62
Oxygen	28·58	
	100·00	100·00

845. The members of this group yield the same products as the members of the preceding group when treated with oxidizing agents, such as MnO_2, or $K_2Cr_2O_7$, and H_2SO_4 (775).

846. These substances also give the same reaction as the members of the previous group with $HgNO_3$, par. 785.

847. The members of this group are especially distinguished by the following properties: they swell and become very translucent in cold water; they dissolve in hot water; on cooling they separate as translucent masses, and are precipitated from the most dilute solutions by chlorine, tannic acid, and most of the salts of the earths and metals.

GELATIN (Glutin).

848. Gelatin in a state of purity is a colourless transparent solid, which is hard, horny, and brittle; it is devoid of taste and smell, and has no action on vegetable colours. It is insoluble in alcohol and ether; it is insoluble in *cold* water, but softens and swells up in it; in *warm* water it dissolves, but the liquid as it cools becomes converted into jelly, gelatinizes, hence the name gelatine; 1 part of pure gelatin dissolved in about 80 parts of water, is sufficient to cause the liquid to gelatinize when it cools. If a solution of gelatin is boiled

for a length of time, it does not gelatinize on cooling; the gelatin appears to be converted by the boiling into an isomeric modification which does not possess the property of gelatinizing.

849. Lime and lime phosphate are much more soluble in a solution of gelatin than in cold water. Common glue always contains a large quantity of lime phosphate, and this substance is considered by Mulder to be an essential constituent of gelatin; and it may be observed that chemical compounds of gelatin and lime phosphate can be prepared.

850. Moist gelatin exposed to the air rapidly putrefies; the liquid at first becomes highly acid, but afterwards gives off a large quantity of ammonia. This property of first becoming acid is characteristic of gelatin.

851. *Action of acids on Gelatin.*—Gelatin is soluble in all the dilute acids with the exception of tannic acid; and it is not precipitated from its solutions by any of the acids except tannic acid.

852. It is dissolved by concentrated H_2SO_4 in the cold without change of colour. The solution diluted with water, and boiled, yields leucine, glycocine (sugar of gelatin), and some other products.

853. When gelatin is boiled with concentrated HNO_3, it becomes gradually converted into oxalic acid, saccharic acid, and two substances resembling suet and tannic acid. When a solution of gelatin in dilute HNO_3 is evaporated, nitrous gas is evolved, and the residue deflagrates just before dryness.

854. Tannic acid is a most delicate test of the presence of gelatin; when it is added to a solution of 1 part of gelatin in 5000 of water, a cloud is evident, and on adding the acid to a strong solution, a dense light coloured precipitate is produced, (tanno-gelatin) which is insoluble in water, alcohol, and ether, but soluble in a warm solution of potash. The composition of the precipitate does not appear to be constant. Tanno-gelatin is identical with *leather*.

855. *Action of chlorine.*—If Cl is passed through a solution

of gelatin, a white pellicle forms round each bubble of the gas, and finally the whole of the gelatin is precipitated in the form of white elastic flakes or filaments. The precipitate is tasteless, slightly acid, imputrescible, insoluble in water and alcohol, but soluble in acids; its compositlon is not known. No similar substance is obtained by substituting Br or I for Cl.

856. *Action of the alkalies.*—A pure solution of gelatin is not precipitated by dilute solutions of the alkalies. When the gelatin solution is boiled with a concentrated solution of KHO it is decomposed into leucine, glycocine and other products. The same change takes place when gelatin is carefully fused with solid KHO.

857. The solubility of lime and its phosphate in solutions of gelatin has already been noticed.

858. *Action of salts.*—"Lead, copper, aluminum, and iron salts, do not produce any precipitates in solutions of gelatin, but if a solution of KHO be added to the mixture of gelatin with alum, or with ferric sulphate, the basic aluminic or ferric sulphate which is formed carries down a large proportion of gelatin."

859. $HgCl_2$ precipitates gelatin from its aqueous solution.

CHONDRIN.

860. Chondrin is transparent, horny, and glistening, it softens to a jelly in cold water, and in warm water it dissolves, but the liquid as it cools gelatinizes. It is insoluble in alcohol and ether. If a solution of chondrin be boiled for a length of time it does not gelatinize on cooling.

861. *Action of acids.*—"Nearly all acids, even organic acids, precipitate chondrin from its aqueous solution. The precipitate formed by hydrochloric, sulphuric nitric, phosphoric, phosphorous, chloric, or iodic acid, redissolves easily in excess of the acid; that formed by sulphurous, pyrophosphoric, hydrofluoric, carbonic, arsenic, acetic, tartaric, oxalic, citric, lactic succinic or tannic acid does not redissolve in excess of the acid employed.

862. "Strong H_2SO_4 dissolves chondrin, forming a syrupy liquid, which, when diluted with water and boiled, yields leucine without glycocine. H_2SO_3 slowly decomposes chondrin. HNO_3, by prolonged action, converts it into xanthoproteic acid.

863. *Action of chlorine.*—" The aqueous solution of chondrin treated with Cl yields a precipitate.

864. *Action of salts.*—" Alum, aluminic sulphate, plumbic acetate and basic acetate, cupric sulphate, ferrous and ferric sulphates, ferric chloride, mercurous and mercuric nitrates, produce copious precipitates in a solution of chondrin, soluble for the most part in excess of the reagent. The precipitates formed by acetic acid, alum and aluminic sulphate, dissolve completely on adding a sufficient quantity of potassic or sodic acetate, or of common salt. The precipitate formed by Fe_23SO_4 redissolves on heating the liquid.

865. "$HgCl_2$ does not precipitate a solution of chondrin; sometimes a slight turbidity is produced, owing apparently to the presence of a little gelatin."

866. *Recapitulation and remarks.*—This group of substances is distinguished from a large number of organic substances by *containing nitrogen.* They are distinguished from the members of the preceding group by potassic ferrocyanide producing no precipitate in their solutions. And their peculiar behaviour with water at once distinguishes them from all other substances.

867. Gelatin is distinguished from chondrin by giving a precipitate with $HgCl_2$.

868. Chondrin is distinguished from gelatin by being coagulated by the vegetable acids such as acetic acid, as well as by alum, and by the neutral and basic lead acetates.

SUGARS.

MILK-SUGAR, GRAPE-SUGAR (Glucose), INOSITE.

869. As milk-sugar, glucose, and inosite, are the chief varieties of sugar met with in the animal kingdom, they are the only sugars we shall notice in this part of the work.

870. The sugars are all soluble in both cold and warm water but they are more soluble in hot water than cold. They all possess a sweet taste; but there are great differences in the relative sweetness of the different varieties.

Sugar of milk (Lactin, Lactose) $C_{12}H_{22}O_{11}H_2O$.

871. This variety of sugar is an animal product, it is found only in the milk of the mammalia, and is the substance which gives the sweet taste to fresh milk. It forms white, translucent four-sided prisms, of great hardness. It is soluble in about six parts of cold, and two parts of boiling water; it does not form a syrup, and has only a feeble sweet taste. It is insoluble in alcohol and ether. Its aqueous solution produces right-handed rotation of a ray of polarized light.

872. It is converted into glucose when boiled with dilute acids. HNO_3 converts it into mucic acid, with a little oxalic acid; it differs from the other sugars, and resembles the gums in furnishing these acids by the action of HNO_3 upon it.

873. It becomes gradually converted in milk, from the influence of the caseous matter, into lactic acid, thus:—$C_{12}H_{22}O_{11}H_2O = 4(H_2C_3H_4O_3)$.

874. Milk-sugar reacts with $CuSO_4$ and KHO, exactly in the same manner as glucose (880).

Grape or Starch Sugar, *Glucose*, $C_6H_{12}O_6H_2O$.

875. Grape-sugar abounds in grapes, figs, plums, and other fruits; it is also formed from starch, cane-sugar, and woody fibre, by processes which will be described under Vegetable Chemistry. It is also a morbid constituent of the urine in the

disease called *diabetes*, its appearance in the urine is the most characteristic feature of the disease.

876. "Glucose crystallizes with difficulty in warty concretions, composed of hard transparent cubes. It forms with NaCl a compound that crystallizes with facility, which is a distinctive character of this variety of saccharine matter.

877. "Glucose is distinguished from cane-sugar by several characters; it is considerably less soluble in water than cane-sugar, though it is more readily taken up by alcohol, and crystallizes from a hot solution of alcohol containing not more than 5 per cent. of water in anhydrous prisms ($C_6H_{12}O_6$). It requires nearly two and a half parts of glucose to produce the same sweetening effect as is produced by one part of cane-sugar. The action of H_2SO_4 upon grape-sugar is quite different from its action upon cane-sugar, as, instead of charring and destroying it as it does cane-sugar, it forms with it a definite compound acid, the solution of which is pale yellow; this acid has been termed sulphosaccharic acid" ($C_6H_{12}O_5SO_3$).

878. Grape-sugar is resolved in contact with yeast or other ferments into alcohol, carbonic acid and water: thus—$C_6H_{12}O_6H_2O = 2C_2H_6O + 2CO_2 + H_2O$.

879. When a solution of grape-sugar is heated with a solution of one of the fixed alkalies it is rapidly decomposed, which is evidenced by the fact that the liquid darkens in colour and finally becomes nearly black. This action of the fixed alkalies on grape-sugar has been proposed as a test for sugar in urine; it is called Moore's test and is employed as follows:—To the suspected urine, an equal bulk of the ordinary solution of KHO is to be added and the whole boiled gently for about five minutes; a deep orange-brown or black colour will be produced if sugar is present. This ought only to be employed as a confirmatory test, as in many cases it might prove very fallacious.

880. The dark brown substance (melassic acid), which is produced when an alkaline solution of sugar is heated, has a very powerful affinity for oxygen, it speedily reduces CuO black oxide to Cu_2O the red oxide when a cupric salt is added

to the alkaline solution of sugar. On this property is founded the most valuable chemical test for sugar which we possess; this is known as Trommer's test. The simplest plan of employing this test is to add a solution of KHO in tolerable excess,* if a precipitate is produced, as is frequently the case in urine, filter and to the filtrate (in a test-tube) add a few drops of a *very dilute* solution of $CuSO_4$.† If sugar is present, the precipitate which first forms is redissolved on shaking, and the fluid becomes of a clear blue colour. This blue solution is then heated to boiling, whereon a yellow cloud (hydrated Cu_2O) forms, which speedily changes to a *red* (the anhydrous Cu_2O) precipitate.

881. When testing urine for sugar by this method the mixture of urine and KHO should not be warmed before the addition of the copper solution, and it ought only to be boiled gently for a minute or two, as several substances besides sugar separate Cu_2O from alkaline solutions of copper if the boiling is prolonged. A counter experiment ought therefore always to be made by leaving at rest one half the mixture of urine, potash, and copper solution, *before it has been warmed*, for six to twenty-four hours without being heated, if sugar is present in the urine a separation of Cu_2O will also take place in this mixture. Sugar is the only substance which can be present in the urine which reduces the copper salt without heat.

882. *Fermentation test.*—Fermentation is frequently employed as a test for the presence of sugar. "When used merely as a qualitative test to indicate whether sugar is or is not present in urine, the following is the simplest way of

---

* An excess of KHO is productive of no harm.

† The solution of the copper salt ought to be so dilute as only to have a faintly blue tinge. Instead of cupric sulphate, Drs. Taylor and Brande recommend cupric tartrate, which is certainly to be preferred to the sulphate; they recommend recently precipitated cupric tartrate to be dissolved in a solution of NaHO or Na_2CO_3. Cupric tartrate is more easily decomposed than the sulphate, less boiling is therefore required, which is a great advantage.

applying it. Fill a test-tube with the suspected urine, having previously mixed with it a few drops of fresh yeast, or still better, a little of the dried German yeast; close the open end with a small saucer or evaporating dish, and while gently pressing the latter upon the tube invert them. A little more of the urine is then poured into the saucer in order to prevent the escape of any of the liquid from the tube, and if any bubbles of air have accidentally been allowed to enter, the exact height of the upper surface of the liquid in the tube must be marked with ink or with a strip of gummed paper. The tube with its contents is then set aside in a warm place having a temperature of about 21° or 27°C., for 24 hours. If sugar is present it begins almost immediately to undergo the vinous fermentation, the CO_2 as it is formed rises in minute bubbles, causing gradual and gentle effervescence, and collects in the upper tube, displacing an equal volume of liquid which escapes through the open end of the tube into the saucer. When the quantity of sugar present is at all considerable, the urine, after fermentation, will be found to possess a faint vinous smell. As bubbles of gas are sometimes given off by the yeast itself, it is a good precaution to put the same quantity of yeast into a second tube of equal size, and fill it up with pure water. The amount of gas, if any, derived from the yeast will thus be rendered apparent, and may afterwards be detected from the volume of gas in the tube containing the urine."—*Bowman.*

Inosite or Phaseomannite $C_6H_{12}O_6$, $2H_2O$.

883. " This sugar occurs in almost all parts of the animal system and is identical with phaseomannite, which occurs in unripe beans, and in many other plants. It forms prismatic crystals of the form of gypsum; it is soluble in water, but insoluble in alcohol and ether; it has a sweet taste; it is not susceptible of the vinous fermentation, but with chalk and cheese it yields lactic and butyric acids. It does not reduce cupric salts. If it be evaporated with HNO_3 nearly to dryness, and then mixed with a little NH_4HO and $CaCl_2$, and

again evaporated, a beautiful rose tint is produced, which is quite characteristic of it."

ALKALOIDS.

UREA, CREATININE, CREATIN.

884. The only bodies we shall notice belonging to this class are the three given in the list; creatin is neutral to test paper, but it has been combined with acids, and has the characters of a weak base. It will be seen that it is closely connected with creatinine. The three substances possess no marked properties which are common to the three.

Urea (CH_4N_2O).

885. "This important compound is an essential constituent of the urine of animals; it is abundant in that of the mammalia and particularly so in the urine of the carnivora; but it has also been met with in the urine of birds and of amphibia. Urea is the principal outlet for the nitrogen of the system, after the materials which compose the animal tissues have experienced oxidation under the influence of the respired air, a healthy human adult excreting about an ounce of urea daily. Urea is not formed in the kidneys; these glands appearing to act somewhat in the manner of filters, by means of which the urea is separated from the mass of the blood, in which it exists already formed before reaching the kidneys."—*Miller.*

886. Urea can be formed *artificially* in a variety of ways; one of the simplest methods for its formation is by evaporating ammonic cyanate (NH_4CNO), which is metameric with urea, at a gentle heat; by a mere alteration of the elements of ammonic cyanate urea is formed as shown in the following equation: $NH_4CNO = CH_4N_2O$.

887. Urea is formed whenever cyanic acid or cyanates come in contact with ammonia or ammonic salts. It is also formed by the spontaneous decomposition of an aqueous solution of

cyanogen. Ammonic cyanate is first formed, and this body becomes converted into urea as the liquid evaporates. It is also formed when ammonia is acted upon by phogene gas ($COCl_2$).

888. Béchamp has recently succeeded in preparing urea from albumen, by subjecting it to the oxidizing action of potassic permanganate.

889. "A solution of urea, *if pure*, may be kept at ordinary temperatures *without alteration*, and it may even be boiled without undergoing decomposition; but if heated in a sealed tube to about 100°, it combines with four equivalents of water and is converted into ammonic carbonate—$CH_4N_2O + 2H_2O = (NH_4)_2CO_3$. The same change takes place slowly at ordinary temperatures in the presence of the mucus of the bladder, the ammoniacal odour acquired by urine after keeping it for a few days being due to this alteration. A similar decomposition into carbonic acid and ammonia occurs when urea is fused with KHO or treated with concentrated H_2SO_4.

890. Cl, when transmitted into an aqueous solution of urea, resolves it into CO_2 and N and HCl: thus, $2CHN_2O + 2H_2O + 3Cl_2 = 2CO_2 + 2N_2 + 6HCl$.

891. Nitrous acid decomposes urea immediately into CO_2, N, and H_2O:—$CH_4N_2O + 2HNO_2 = CO_2 + 2N_2 + 3H_2O$.

892. Urea crystallizes in flattened four-sided prisms; they generally resemble KNO_3 in appearance, and have a similar cooling, saline taste; they are inodorous. They are soluble in their own weight of cold water and in every proportion in hot water; they dissolve in 4·5 of cold and in two parts of boiling alcohol; but they are insoluble in ether, and in an excess of strong nitric acid. Its solution is neutral to test-paper.

893. Urea is basic in its characters, although neutral to test-paper; it combines with acids to form salts, some of which are crystalline. "Of these, the two which are of the most practical importance, are the oxalate ($2CH_4N_2O, H_2C_2O_4$), and the nitrate (CH_4N_2O, HNO_3), which, on account of their sparing solubility in water, supply a ready means of separating urea from the other matters co-existing in the urine.

894. "*Oxalate of urea* may be prepared by concentrating urine on a water-bath to about one eighth of its bulk, and filtering through muslin, in order to separate the insoluble sediment of phosphates and urates, which are gradually deposited during the evaporation. The liquid thus clarified, is mixed with about an equal bulk of a strong solution of oxalic acid in hot water, or the solid acid in powder may be added as long as the liquid, heated to about 88° or 94° C., continues to dissolve it. The mixture, on cooling, deposits an abundant crop of crystals of oxalate of urea, mixed with a little of the excess of oxalic acid, and coloured brown by the adhering impurities. The crystals are then gently pressed between folds of filtering paper, washed with a small quantity of ice-cold water, and purified by recrystallization; the last traces of colouring matter being removed, if necessary, by boiling the solution with animal charcoal. The oxalate thus obtained is colourless, and in the form of tabular or prismatic crystals, which are readily soluble in hot water, but only sparingly so in cold, 25 parts of which dissolve not more than 1 part of the salt.

895. "*Nitrate of urea* may be obtained by adding strong colourless HNO_3, free from HNO_2 (891), to urine previously concentrated by evaporation to about one third its bulk; the nitrate gradually separates in irregular rhomboidal plates, more or less coloured and modified in form by the impurities present. The crystals are washed with a little ice-cold water, then pressed between folds of filtering paper, and redissolved in lukewarm water; lastly, they are purified by recrystallization, and, if necessary, the last traces of colouring matter may be removed by boiling the solution with animal charcoal. It is soluble in about 8 times its weight of cold water, and in a much smaller quantity of hot. It is tolerably soluble also in alcohol, especially when warm, but almost insoluble in ether.

896. "The formation of this crystalline compound on the addition of HNO_3, is one of the most distinctive tests for the presence of urea which we possess. The experiment is made

easily, and with great delicacy, under the microscope, by concentrating a drop or two of urine on a glass slide, and adding to it about an equal quantity of pure HNO_3; the nitrate will gradually crystallize in delicate rhomboidal plates, the number and abundance of which will furnish some indication of the quantity of urea present in the secretion."*

CREATININE ($C_4H_7N_3O$).

897. This substance is a powerful organic base; its aqueous solution restores the blue colour to reddened litmus paper, and when heated with solutions of ammonic salts it expels the ammonia like the fixed inorganic alkalies. It forms colourless prismatic crystals, and its salts are also crystalline. It dissolves in about 12 parts of cold water; it is much more soluble in hot water; it is very soluble in boiling alcohol, but much less so in cold alcohol, it therefore crystallizes out as the boiling solution cools.

898. It has a strong tendency to form basic double salts; example: if a solution of $AgNO_3$, moderately concentrated, be mixed with one of creatinine, it becomes converted into a magma of white needles, which are very soluble in boiling water, and it forms a similar compound with a solution of $HgCl_2$. On the addition of a concentrated solution of $ZnCl_2$ to a solution of this base, a double compound $(C_4H_7N_3O)_2ZnCl_2$ is precipitated in a crystalline form; when very slowly formed the crystals are distinctly prismatic, but when quickly produced, and as seen under the microscope, fine needles are observed concentrically grouped together, forming either perfect rosettes, or tufts which cross each other, or of which each two are connected by thin short stalks, so as to resemble brushes passing one into the other. As $ZnCl_2$ is the test usually employed to detect this base, it is important to observe that the double compound of zinc and creatinine is not precipitated on the addition of the zinc chloride to the creatinine chloride; but that the separation at once takes place, if before

---

* Bowman's 'Medical Chemistry.'

the addition of the $ZnCl_2$ solution, a sufficiency of sodic acetate is mixed with the creatinine salt.

899. This base has been found in the juice of muscle, in the blood as well as in the urine. Creatin is converted into creatinine by the action of strong acids.

CREATIN ($C_4H_9N_3O_22H_2O$).

900. In its pure state, this substance forms brilliant, colourless, prismatic crystals, which become dull by loss of water at 100° C. It has a bitter, pungent taste. It dissolves in 75 parts of cold water. Boiling water takes up a much larger quantity of it, but as it cools, the creatin separates in the crystalline form. Alcohol takes up only one part in 9410 parts; and in ether it is completely insoluble. In an impure state the solution readily putrefies.

901. It dissolves without change in dilute mineral acids; but when boiled with concentrated acids, it gives off water, and is converted into creatinine:—$C_4H_9N_3O_22H_2O - 3H_2O = C_4H_7N_3O$.

902. $ZnCl_2$ produces no precipitate with perfectly pure creatin; but if creatinine is present, a triple compound consisting of chloride of zinc, creatin and creatinine, is precipitated in the form of radiating crystals.

903. This substance is found in the juice of muscles; and it is also found in the urine.

ACIDS.

LACTIC ACID, HIPPURIC ACID, GLYCOCHOLIC ACID, HYOCHOLIC ACID, TAUROCHOLIC ACID.

904. These acids are grouped together simply on account of their acid character.

LACTIC ACID $H_2C_3H_4O_3$.

905. There are two modifications of this acid, the one called *ordinary* lactic acid, is formed by the fermentation of milk

cane, and grape sugars; it is also found in vegetable matters which have turned sour. The other modification called sarcolactic or paralactic acid exists in muscular flesh.

906. The ordinary lactic acid in its most concentrated state is a colourless, inodorous, thick, syrupy fluid, which cannot be solidified by the most intense cold; its specific gravity = 1·215, it dissolves readily in water, alcohol, and ether, attracts water from the atmosphere, has a strongly acid taste and reaction, decomposes when heated, and displaces not only volatile acids, but even many of the stronger mineral acids from their salts.

907. With bases lactic acid generally forms neutral salts, all of which are soluble in water, and many in alcohol, but none in ether. Most of the lactates may be heated to 150° or 170° and some even to 210°, without undergoing decomposition.

908. Sarcolactic acid is hardly distinguishable from ordinary lactic acid; the difference between the two is mostly distinctly marked in the calcic and zinc salts. If sarcolactic acid be heated for a long time to 130° or 140°, it is converted into the anhydride, which, when boiled with water, is converted into ordinary lactic acid.

HIPPURIC ACID OR BENZAMIDACETIC ACID, $HC_9H_8NO_3$.

909. This acid occurs in combination with K or Na in large quantity in the urine of herbivorous animals, and in smaller quantity also in human urine.

910. This acid, when treated with nitrous acid, undergoes the decomposition peculiar to amidogen compounds, viz. the formation of a non-nitrogenous acid, water, and the liberation of nitrogen. The acid formed on treating hippuric acid with nitrous acid, is benzo-glycolic acid ($C_9H_8O_4$). Under the influence of boiling water benzo-glycolic splits up into benzoic and glycollic (oxyacetic) acids.

911. When hippuric acid is boiled for some hours with con-

centrated HCl, it assimilates the elements of water and is resolved into benzoic acid and amidacetic acid or glycocine :—

$$\underbrace{HC_9H_8NO_3}_{\text{Hippuric acid.}} + H_2O = \underbrace{HC_7H_5O_2}_{\text{Benzoic acid.}} + \underbrace{HC_2H_4NO_2}_{\text{Glycocine.}}.$$

912. Hippuric acid has been artifically made by acting upon the zinc salt of glycocine with chloride of benzoyl :—

$$Zn(C_2H_4NO_2)_2 + 2C_7H_5OCl = ZnCl_2 + 2HC_9H_8NO_3.$$

913. This acid crystallizes in rhomboidal prisms, or in thin plates. It is sparingly soluble in cold water, one part requiring 400 parts for its solution; but it is very freely soluble in hot water. It is readily soluble in alcohol; but only sparingly soluble in ether, which distinguishes it from benzoic acid (579). Exposed to a high temperature it is decomposed into hydrocyanic acid, benzoic acid, ammonic benzoate, and other products. Heated with a fragment of KHO it disengages NH_3. If placed in contact with ferments, it undergoes a kind of fermentation, the products of which are benzoic acid and ammonia.

914. Owing to this speedy conversion of it into benzoic acid and ammonia by ferments, it is not surprising that if the urine becomes in the slightest degree putrid, it is speedily decomposed into benzoic acid and ammonia. On the other hand, when benzoic acid is taken into the system, it is converted into hippuric acid, and is found in the urine in that state.

Glyco-cholalic acid or Glycocholic Acid (*Cholic acid* of Strecker) $HC_{26}H_{42}NO_6$.

915. This acid, in combination with the fixed alkalies, exists in the bile of man and other animals, but it is present in the greatest quantity in ox-bile. The acid is a white crystalline solid; it has a strong acid reaction, and a bitterish-sweet taste. It is more soluble in hot water than cold; alcohol dissolves it freely, but leaves it as a resinous mass on evaporation; it is

very sparingly soluble in ether. The salts which it forms with the alkalies and alkaline earths may be crystallized; they are soluble in alcohol.

916. When this acid is boiled with an alkaline solution, as solution of KHO or BaH_2O_2, it is decomposed into glycocine (amidacetic acid), and a non-nitrogenous acid, called cholalic acid* (the cholic acid of Demarçay):—

$$\underbrace{HC_{26}H_{42}NO_6}_{\text{Glyco-cholalic acid.}} + H_2O = \underbrace{HC_{24}H_{39}O_5}_{\text{Cholalic acid.}} + \underbrace{C_2H_5NO_2}_{\text{Glycocine.}}.$$

917. When it is boiled with concentrated H_2SO_4 or HCl, it is split up into glycocine and choloidinic acid ($C_{24}H_{38}O_4 =$ cholalic acid $-$ 1 eq. of water); if the ebullition with the acids be continued, the choloidinic acid is decomposed into a resinous substance, called, from its insolubility in water, *dyslysin* ($C_{24}H_{36}O_3$), and water.

GLYCO-HYOCHOLIC ACID, $HC_{27}H_{42}NO_5$.

918. Pig's bile differs from the bile of other animals, inasmuch as it contains glyco-hyocholic acid instead of glycocholalic acid; the former acid is decomposed like the latter by alkaline solutions and acids and into substances of analogous composition.

919. When it is boiled with an alkaline solution, it is decomposed for instance into glycocine and hyocholic acid:—

$$\underbrace{HC_{27}H_{42}NO_5}_{\text{Glyco-hyocholic acid.}} + H_2O = \underbrace{HC_{25}H_{39}O_4}_{\text{Hyocholic acid.}} + \underbrace{C_2H_5NO_2}_{\text{Glycocine.}}.$$

920. When it is boiled with acids it is decomposed into glycocine and a substance homologous with dyslysin, which is termed hyodyslysin ($C_{25}H_{38}O_3$).

---

* This acid is soluble in H_2SO_4, and on the addition of a drop of this acid and a solution of sugar (one part of sugar to four of water) a purple-violet colour is produced which constitutes Pettenkofer's test for bile.

TAUROCHOLALIC ACID OR TAUROCHOLIC ACID (*Choleic Acid* of Strecker) $HC_{26}H_{44}NSO_7$.

921. The bile of man and most animals, with the exception of the ox and pig, consists mainly of taurocholalate of soda or potash. The alkaline salts of this acid are very soluble in water and alcohol. They give no precipitate with neutral lead salts, but with the basic salts they deposit a plaster-like compound, which is soluble in boiling water. They yield with H_2SO_4 and sugar a violet colour similar to that produced by the cholates.

922. When this acid is boiled with alkaline solutions it is decomposed into cholalic acid and taurine:—

$$\underbrace{HC_{26}H_{44}NSO_7}_{\text{Taurocholalic acid.}} + H_2O = \underbrace{HC_{24}H_{39}O_5}_{\text{Cholalic acid.}} + \underbrace{C_2H_7NSO_3}_{\text{Taurine.}}.$$

923. When it is boiled with acids it is decomposed into taurine * and choloidinic acid or dyslysin, according to the duration of the experiment (917).

CYSTINE, XANTHINE, AND CHOLESTRIN.

924. These three substances are met with in *calculi*.

925. CYSTINE or Cystic Oxide ($C_3H_7NSO_2$).—This substance is met with nowhere but in the urine; it was originally discovered by Wollaston in a urinary calculus; calculi of this nature, although very rare, have since been found by many other chemists. "It occurs in colourless, transparent, hexagonal plates or prisms; it is devoid of taste and smell, and is insoluble in water and alcohol. It dissolves in oxalic and the mineral acids, forming with them saline combinations, most of which are crystallizable, but it does not unite with acetic,

---

* The student is referred to the author's 'Second Step in Chemistry,' page 525, for an account of Kolbe's important experiments on the constitution of taurine.

tartaric, or citric acid; it is decomposed by nitric acid, leaving, on the evaporation of the fluid, a reddish-brown mass; it dissolves freely in the caustic fixed alkalies and their carbonates. It dissolves in NH_4HO, but does not unite with it, so that on evaporation it crystallizes unchanged. It is insoluble in $(NH_4)_2CO_3$; hence it is best precipitated from its acid solutions by $(NH_4)_2CO_3$, and from its alkaline solutions by acetic acid.

926 " Cystine does not fuse on the application of heat, but it burns with a *bluish-green flame*, developing at the same time a very peculiar acid odour; on dry distillation it develops a stinking empyreuma and ammonia, and leaves a voluminous porous coal. On boiling it with alkalies, ammonia is first developed, and subsequently an easily inflammable gas, which burns with a blue flame.

927. " Cystine is characterised by the readiness with which it crystallizes in well-formed hexagonal plates, which may be distinguished with great ease under the microscope, and by its solubility both in alkalies and mineral acids. Further, it may be known by the peculiar odour which it develops on dry distillation and on burning, which is unlike that evolved by any other similar substance. Liebig has given the following test for cystine. The potash-extract of the substance in which we are searching for cystine must be decomposed with a solution of PbO in KHO; if, on the application of heat, there be a precipitation of PbS, cystine is probably present; we must, however, previously satisfy ourselves that no other organic substance containing sulphur, as for instance, albumen, mucus, &c., be simultaneously present.

928. "If cystine be mixed with a small quantity of the urates, the two substances may be separated by the aid of boiling water, in which the former is insoluble. Uric acid occasionally appears under the microscope in the form of hexagonal tablets, but we should never trust in these cases to microscope examination alone."—*Lehmann.*

929. XANTHINE OR XANTHIC OXIDE ($C_5H_4N_4O_2$).—This substance has also been named *uric oxide* and *urous acid* owing

to its being regarded as uric acid in a lower stage of oxidation. It is the principal constituent of a very rare variety of urinary calculus. It is one of the products in the decomposition of guanine, a substance found in guano and in the excrement of the garden spider. It is likewise present in nearly every part of the animal organism, and, although in very minute quantities, in urine. It is a white amorphous powder, and it acquires a waxy lustre on friction with a hard body. It is very slightly soluble in water; it is insoluble in alcohol and ether. It dissolves easily in ammonia. It also dissolves freely in the fixed alkalies; carbonic acid separates it from its alkaline solution. It is all but insoluble in HCl and $H_2C_2O_4$; it is soluble in H_2SO_4 and HNO_3. It dissolves in HNO_3 without disengagement of gas, and gives on evaporation a yellow residue, which, on addition of NH_4HO or KHO, turns yellowish red. From the circumstances under which it occurs it can only be confounded with cystine or uric acid; it differs from these by its amorphous condition. It is distinguished from cystine by its insolubility in HCl and $H_2C_2O_4$. It is distinguished from uric acid by its solubility in NH_4HO, and by the residue obtained on evaporating its HNO_3 solution not turning red on the addition of NH_4HO (617).

930. CHOLESTRIN $C_{26}H_{44}O$.—"This substance is found in small quantity in various parts of the animal system, as in the bile, in the brain and nerves, and in the blood. It forms the chief ingredient of *biliary calculi*, from which it is easily extracted by boiling the powdered gall-stones in strong alcohol, and filtering the solution while hot; on cooling the cholestrin crystallizes in brilliant colourless plates. It has the physical characters of a fat, is insoluble in water, tasteless and inodorous; it is freely soluble in boiling spirit and also in ether. It is not saponified by potash; thus differing from other fatty and oily substances which it resembles in many respects. It melts at 137°, and sublimes at 200° C."

COLOURING MATTERS.

931. We group together the colouring matter of the urine, the bile, and the blood.

932. *Colouring matter of the urine.*—"The colouring matter of the urine is constantly undergoing change; by means of neutral and basic lead acetate it may be separated into two substances which contain different amounts of carbon. The substance which contains most carbon may be obtained as a dark-blue powder; when dry it has a copper colour like indigo and dissolves in alcohol, giving a purple-blue solution. It is said to occur most evidently in Bright's disease. Virchow states that he met with this blue pigment in crystals in unhealthy urine." Thudicum believes there is only one *normal* urinary pigment which he has named *urochrome*, an amorphous substance of a pure yellow colour; Schunk believes there are two.

933. *Colouring matter of the bile.*—The principal colouring matter of the bile has been called *cholepyrrhin* or *bilirubine* ($C_{16}H_{18}N_2O_3$). When dry it is reddish brown and uncrystallizable, insoluble in water, slightly soluble in alcohol and ether, easily soluble in chloroform and in solutions of the alkalies. The colour of these solutions is yellow or orange; if to the alkaline solution is added an equal volume of alcohol and then fuming nitric acid charged with nitrous vapours, it passes through *green, blue, violet,* and *red;* after some time it again turns yellow; this reaction is very delicate.

934. Another colouring matter has been called *biliverdin.* It is dark green, amorphous, without taste or smell, insoluble in water, slightly soluble in alcohol, but soluble in ether.

935. *Colouring matter of the blood.*—The red colouring matter of the blood-corpuscles is called hæmatin or hæmatosin; it leaves when burnt a residue of ferric oxide and calcic phosphate. It is unaffected by dilute NH_4HO, but is entirely

destroyed by ebullition, with the formation of a dirty-coloured coagulum, which dissolves in KHO with an indistinct greenish colour.

936. *Tests for blood.*—" Blood-stains on articles of clothing may be identified—1. By their peculiar crimson-red colour. 2. By the shining and raised surface of the stain or spot (dried albumen and fibrin). 3. By their ready solubility in water to which they give a red colour. The water under these circumstances contains albumen as well as hæmatosin. Weak ammonia does not change the red colour to a *blue*, *green*, or *crimson* tint. When boiled, the albumen and hæmatosin are both coagulated, and the red colour is entirely destroyed; a muddy brown coagulum subsides which is quite insoluble in water and alcohol." 4. Bloxam has proposed the following test, which is very delicate. A mixture of tincture of guaiacum and oxonized ether (that is a solution of hydric peroxide (H_2O_2) in ether); this mixture instantly produces with blood or blood stains a beautiful *blue tint*. For the examination of such stains in a dry state, an inch power of the microscope will be found convenient.

937. " By employing a small quantity of water on a glass slide in order to dissolve the stain, the clot may be broken up and the red corpuscles separated. These may be examined by a quarter-inch power under the microscope. When detected, the evidence of the presence of blood is placed beyond doubt. No other red colouring matter, vegetable or animal, owes its colour to corpuscles or cells. A small quantity of glycerine added to the water which is used as a solvent prevents it from drying too rapidly."—*Brande and Taylor.*

938. *Test for bile.*—Bile is essentially composed of soda salts of the two acids, glycocholic and taurocholic, cholestrin, mucus, and colouring matter. It is a ropy, viscid, and saponaceous liquid of a greenish-yellow colour in man, greenish brown in the ox, and emerald or grass-green in birds, reptiles and fish. It has a bitter taste and an offensive odour. Its reaction is generally alkaline, it is sometimes neutral but never acid, excepting in peculiar states of disease. It mixes in all

proportions with water, it is not coagulated by heat. Alcohol renders it turbid by precipitating the mucus.

939. We have noticed (par. 921 and note page 320) that the two acids in the bile when treated with sulphuric acid and sugar acquire a purple colour. Upon this reaction a test, called Pettenkofer's test, for bile has been founded. The best mode of applying the test for the detection of small quantities of bile in blood or other animal fluids is as follows:—The alcoholic extract of the liquid to be tested for biliary matter is dissolved in a little water and mixed with a single drop of a solution of sugar (one part of sugar to four parts of water), and pure strong H_2SO_4 is then added in small quantities till the turbidity at first produced disappears, cooling after each addition; it then for a few moments exhibits a yellowish colour, which, however, soon changes to a pale cherry-red, then to deep carmine, then to purple, and finally to an intense violet tint. For the success of the experiment, care must be taken not to add too much sugar, otherwise a black mass will be formed which will completely mask the reaction. The temperature of the mixture must be allowed to rise to about 50° C., but not higher. The reaction takes place with any kind of sugar and likewise with acetic acid.

A METHOD FOR ANALYSING QUALITATIVELY ANIMAL SECRETIONS.*

940. The physical characters, such as colour, taste, odour, consistence, &c., should first be carefully observed. The specific gravity may also be ascertained, when it can conveniently be done, as a knowledge of the density of the fluid will serve to furnish some indication of the amount of solid matter held in solution.

941. The liquid should be examined by test-papers whether it is neutral, alkaline, or acid.

---

* The method for analysing the animal secretions, and for the analysis of urine, has been taken mainly from Gerhardt and Chancel's 'Qualitative Analysis.'

942. When the liquid holds in suspension any solid or semi-solid matter the dissolved should be separated from the undissolved portion either by decantation or by filtering it through paper or fine muslin. The microscopic examination of the residue generally furnishes some useful indications. The spontaneous coagulation in a secretion, at first limpid, is due almost always to fibrine.

943. The clear liquid is then submitted to the following examinations :—

944. *First examination.*—We heat a portion of the liquid in a test-tube; when the liquid is neutral or alkaline, one or two drops of acetic acid is first added to produce a *faint acid reaction.* If the liquid remains clear on warming it, we can be certain of the absence of albumen; in that case we pass on to the *second examination* (948).

945. If, on the contrary, the liquid becomes troubled or coagulated, it becomes necessary, after having agitated it, to divide it into two portions. To one portion add a few drops of dilute HCl; if the precipitate disappears it has not been due to albumen but was probably due to calcic or magnesic phosphate, or both. The other portion of the liquid must be examined by the microscope.

946. When the dilute HCl does not redissolve the precipitate, we then add a larger quantity of it and finally boil the mixture; if the precipitate becomes slowly dissolved and the liquid assumes a violet colour (780), this reaction indicates the presence of *albumen.* We control this result by examining the action of nitric acid upon the primitive secretion (779 and 804).

947. If the coagulum formed by boiling the liquid, or the liquid itself has a reddish tinge *hæmatine* and also *globulin* may be present. In this case, we dry the coagulum; it then assumes a brown or black tint. It is afterwards boiled with alcohol to which a little H_2SO_4 has been added; if it contains hæmatine, the liquid is coloured red, and the alcoholic extract after having been evaporated to dryness furnishes a residue which gives after calcination, the reactions of iron (935).

948. *Second examination.*—A liquid which does not contain albumen, or from which it has been separated by coagulation and filtration, may yet contain the following albuminoidal substances, *casein*, *globulin*, *glutin*, *chondrin*, *pus*, and *mucus*, and possibly *paralbumin* and *metalbumin*.

949. A sample of the liquid is mixed with potassic ferrocyanide. If it remains clear, casein and globulin are absent (784), pass on to the third examination (par. 951).

950. If a precipitate is formed, test for casein with solution of $CaCl_2$, and boil the mixture, which becomes turbid if casein is present (842). When this effect is manifested digest the liquid with rennet at a temperature of 40° C. in order to render the coagulation of the caseine complete. If globulin is present the liquid will be rendered turbid by the addition of a few drops of acetic acid, and give afterwards a flaky precipitate when neutralized with NH_4HO (836).

951. *Third examination.*—To a portion of the liquid add acetic acid. If it remains clear *pus*, *mucus*, and *chondrin*, are absent; pass on to the fourth examination (par. 953).

952. A precipitate is formed; test the solution with $HgCl_2$, if no precipitate is formed *pus* is absent. If the $HgCl_2$ produces merely a turbidity, *mucus* or *chondrin* is, perhaps, present. Concentrate a portion of the liquid; the formation of a jelly indicates *chondrin* (860), the presence of which may be confirmed by its behaviour with alum and metallic salts (864).

953. *Fourth examination.*—The liquid in which acetic acid produced no precipitate may yet contain glutin. Concentrate a portion strongly and leave it to cool; the formation of a jelly will indicate glutin, which may be further tested with $HgCl_2$ (859).

954. *Fifth examination.*—The original liquid, or if it contained albumen, the liquid freed from that compound by boiling is concentrated by a gentle heat to a half or one third of its volume, and is then left to cool; if no precipitate forms, the *urates* are probably absent. Pass on to the *sixth examination*.

955. If a precipitate is formed add acetic acid. If the *deposit previously amorphous* is seen (after the addition of

the acid), under the microscope, to assume the form of rhombic tablets *uric acid* is indicated; confirm its presence by dissolving the deposit in HNO_3 and examining it for uric acid as directed in par. 617.

956. *If the deposit is crystalline* and does not change its form by acetic acid, it points to the presence of *calcic sulphate* or *magnesic phosphate;* the presence of these salts must be confirmed by their reactions. The precipitate, if crystalline, may also contain *benzoic acid, calcic hippurate, tyrosine,* and *allantoin.*

957. *Sixth examination.*—The concentrated liquid in which no precipitate is formed by boiling and subsequent cooling, or the liquid filtered from such a precipitate, is evaporated to a syrup on the water-bath and left to itself for a considerable time. If crystals gradually form, it is left to stand as long as they continue to increase. They may consist of *creatine, creatinine, glycocine, leucine, allantoin, taurine, sarcosine, inosite, alkaline hippurate, sodic chloride,* and *other inorganic salts.*

958. It must in the first place be determined whether these crystals are organic or inorganic. In the former case they must be tested especially for *nitrogen, sulphur,* and *phosphorus* (749, 750, 754), their chemical nature determined as nearly as possible, and the further examination regulated accordingly. If inorganic they must be examined according to the usual methods. If they blacken when strongly heated, but also leave a fixed residue, they probably consist of an organic acid, combined with an inorganic base; in that case the fixed residue will effervesce strongly with acids.

959. The syrupy residue itself, or the liquid, separated from the crystals which have formed in it, is evaporated nearly to dryness on the water-bath, and the residue is digested with alcohol of a sp. gr. of 0·83. The alcoholic solution and the substance insoluble in alcohol are separately examined.

960. *The alcoholic solution* is submitted to the following examinations:

1. To a small portion of the alcohol solution concentrated

and then diluted with water, is added drop by drop, fuming nitric acid (containing nitrous vapours); if there is formed after the addition, at the bottom of the liquid a zone at first green, next blue, violet, red, and lastly of a dirty yellow, it proves the presence of the *colouring matter of the bile* (933).

2. Another portion also concentrated and then diluted with water is mixed with sugar and H_2SO_4; a beautiful purple red colour proves the presence of the *acids in the bile* (939).

3. In a third portion, we look for *glucose*. This substance generally communicates to the liquid a sweet taste. This portion of the alcoholic solution is evaporated to dryness on the water bath, the residue is redissolved in water and examined for glucose by the copper test (880 and 881). The result ought to be controlled by the fermentation test (882).

4. The greater part of the alcoholic solution is evaporated to a very small volume, it is then mixed with *pure* nitric acid, which must be free *especially* from nitrous acid, and we place the vessel in a cooling mixture. If a crystalline deposit is formed, it is examined by the microscope to ascertain whether it has the appearance of nitrate of urea* (895 to 897) or of hippuric acid or benzoic acid. The indications obtained by the microscope are confirmed by the chemical reactions.

5. A portion of the *concentrated* alcoholic solution is mixed with a syrupy solution of $ZnCl_2$; if a precipitate is not formed even after a length of time, the liquid does not contain creatinine (898). If a precipitate is produced, we submit it to some special examinations, to ascertain the presence of creatine as well as creatinine (902).

6. Lastly, if the alcoholic solution possessed a strong acid reaction, it has still to be examined for lactic acid. To effect this the extract is concentrated and heated along with oxide or carbonate of zinc; a drop of the boiling filtered liquid is placed betwen two plates of glass, and we examine it by the microscope to see if the characteristic crystals of lactate of zinc are formed (908).

---

* Care must be taken not to confound the alkaline nitrates for nitrate of urea.

961. *Insoluble residue.*—In addition to *mucus* and undefined *extractive matters,* this residue can contain uric acid, a little casein, &c.

962. *Seventh Examination.*—After having finished the previous examinations, a portion of the *original* solution is evaporated to dryness on the water bath and the residue treated with ether. This dissolves the fatty matters, the presence of which we ascertain by evaporating the ethereal solution.

963. The portion insoluble in ether must be incinerated in a platinum crucible, and the inorganic salts determined by the ordinary methods.

QUALITATIVE ANALYSIS OF URINE.

964. The preceding method can, with some slight modifications be applied to the analysis of most of the animal secretions.

965. Of the secretions, the urine presents a particular interest for the medical practitioner, owing to the changes which it undergoes in its composition by the effects of certain diseases, and which can be made use of as a means of diagnosis.

966. The bodies which normal urine holds in solution in water are:

Organic Substances.	*Mineral Substances.*	
Urea.	Potassic	Salts.
Uric acid.	Sodic	
Hippuric acid.	Calcic	
Creatine.	Magnesic	
Creatinine.	Iron	
Colouring and extractive matters.	Silicates.	
	Phosphates.	
Mucus of the bladder (in suspension).	Sulphates.	
	Chlorides.	

967. We find in addition, in normal urine, very small quantities of ammonia and of carbonic acid gas.

968. Recently emitted, it always possesses an acid reaction,* due very probably to the presence of hippuric or uric acid. It behaves with reagents in the following manner:

1. It is not coagulated by *boiling*.

2. The *caustic alkalies*, on being added to it, produce a turbidness, or a precipitate of the phosphates of the alkaline earths.

3. $BaCl_2$ gives a precipitate of baric sulphate and phosphate.

4. $AgNO_3$ gives a precipitate of argentic chloride and phosphate.

5. *Lead acetate* gives a precipitate of plumbic phosphate, sulphate and chloride.

6. $(NH_4)_2C_2O_4$ gives a precipitate of calcic oxalate.

7. *Alcohol* determines a turbidness which disappears by the addition of a sufficient quantity of water.

969. The following substances are only contained in the urine in certain diseases:

1. Ammonic carbonate. Lactic acid. Albumen (in many diseases). Fibrine (found only in the sediments). Fatty substance (very rarely). Colouring matter of the bile (in liver complaints). Acids of the bile rarely. Glucose (diabetes). Sulphuretted hydrogen (very rarely). Calcic oxalate and cystine.

970. Before proceeding to the examination of the substances contained in the urine, it is necessary to observe the colour, the transparency, the odour, the action upon test-paper. When the urine possesses an alkaline reaction, it is necessary to note if it is fresh, or if it is already commencing to undergo putrefaction.

971. It is equally useful to determine its density; the density of healthy human urine varies from 1,005 to 1,030.

972. After having obtained this preliminary information, we allow a quantity of the urine to stand for some time in

---

* The experiments of Dr. Bence Jones show that when passed shortly after eating, the urine is often neutral, or even alkaline, becoming again gradually more and more acid up to the time when the next meal is taken.

order to allow time for the formation of a sediment. We then filter and examine separately the filtrate and the sediment.

973. *The filtrate.*—A quantity of the urine is boiled in order to coagulate the albumen * when it is present, after that we examine the filtered liquid as described in par. 954. We at first look for the normal constituents of the urine, such as uric acid, the urates, hippuric acid, and urea; lastly those which are accidental, as ammonic carbonate, lactic acid, the colouring matter of the bile and glucose.

974. Ammonic carbonate can only be present in urine which has an alkaline reaction. The urine, which contains this ammonic salt, effervesces on the addition of an acid; when the urine is boiled with KHO, NH_3 is disengaged, and is recognised by its reactions (24).

975. Urine containing biliary matter is in general strongly coloured; its tint varies from saffron yellow, to yellowish brown; if the urine has a sediment, this is also coloured. When we agitate a sample of this urine, there is formed on the surface a yellow scum.†

976. Urine containing sugar is usually characterised by its high specific gravity, which is frequently from 1,030 to 1,045, and occasionally as high as 1,050 and 1,055. If, however, the sugar is present only in small quantity, the specific gravity may not be higher than usual; so that a moderately low specific gravity is of itself no proof of the absence of sugar. It is generally paler in colour than normal urine; and it is generally slightly turbid.

977. Urine containing fatty or chylous matter, is usually

---

* The precipitate produced by boiling is not a sure proof of albumen; since a white precipitate is also produced by boiling, when the urine (free from albumen) contains an excess of earthy phosphates; see pars. 945 and 946 for distinguishing the two precipitates.

† The taste of urine containing biliary matter is remarkably bitter, a peculiarity which furnishes a ready indication of its presence when other tests are not to hand; though it must not be implicitly relied on, since small traces may exist in the secretion without communicating to it any very decided taste (Bowman).

more or less turbid, and frequently has an almost milky appearance.

978. Urine containing sulphuretted hydrogen, has the odour of rotten eggs; test for it as directed in par. 468.

979. *Sediments.*—The sediments ought to be examined microscopically as well as chemically.

980. The bodies contained in urinary sediments are—

Uric acid; the urates of lime, magnesia, potash, soda, and ammonia. Calcic oxalate. Calcic phosphate and magnesic ammonic phosphate. Cystine. Different organic materials, such as mucus, blood, pus, spermatozoa, &c.

981. Free uric acid is only found in the sediments furnished by dark-coloured urine, and it possesses a distinct acid reaction. These sediments are also coloured; they can have a pale tint, but it is generally yellow, orange yellow, or brown; they have a granular appearance, and frequently even visibly crystalline to the naked eye. The uric acid can be very well detected with the microscope, or by its reaction with HNO_3 and NH_4HO (617). It is distinguished from the urates by its insolubility in water, and by the fixed residue which these leave on incineration; it is distinguished from urate of ammonia by the latter disengaging ammonia in contact with KHO.

982. The urates also form a part of the sediments deposited from acid urine. The colour of these sediments, as well as the urine, varies much. The urates contained in the sediments present frequently, to the naked eye, the appearance of mucus, of pus, and of blood, and can be distinguished only from these matters by microscopic observation and chemical analysis. Sodic urate is the one most frequently met with.

983. Calcic oxalate can make part of the sediment furnished by urine, the reaction of which is acid, neutral or alkaline, and it is not rare to find it associated with the urates. The urine containing calcic oxalate possesses a coloration, sometimes clearer, sometimes darker, than that of normal urine; its colour is frequently that of amber yellow. Calcic oxalate, obtained by double decomposition, is an amorphous powder, whilst that found in the urinary sediments is distin-

guished by its crystalline form. The identity of calcic oxalate is easily determined by the aid of its chemical reactions; when it is heated upon platinum foil, it is transformed into calcic carbonate without carbonization.

984. The phosphates of the alkaline earths are easily identified by the chemical reactions. (*See* par. 198.)

ANALYSIS OF CALCULI AND CONCRETIONS.

985. The number of substances which compose the calculi and concretions of animals is not considerable; the most frequent are:

Uric acid and the urates.
Xanthine.
Cystine.
Ammonic hippurate.
Calcic phosphate.
Magnesic ammonic phosphate.
Calcic oxalate.
Calcic carbonate.
Magnesic carbonate.
Cholesterin (with other fatty matters).
Colouring matter of the bile.
Fibrine.

986. The preceding substances are accompanied by the following bodies:

The acids of the bile.
Albumen.
Mucus.
Extractive matters.
Soluble salts.

987. The manner in which calculi comport themselves when calcined upon platinum foil by the aid of heat, permits of their division into many groups:

CALCULI WHICH DO NOT LEAVE A FIXED RESIDUE.

988. *Calculi entirely combustible.*—They can be formed of uric acid, of ammonic urate, ammonic hippurate, of xanthine, of cystine, of cholesterin, of the colouring matter of the bile, of fibrine, or of albumen.

CALCULI WHICH LEAVE A FIXED RESIDUE.

A. *Calculi partially combustible.*—They can contain sodic urate, calcic urate, and all the organic matters quoted in combination with mineral substances.

B. *Calculi entirely fixed.*—They cannot contain any organic matter.

989. CALCULI WHICH DO NOT LEAVE A FIXED RESIDUE.—We treat a portion of this material with concentrated HNO_3, we evaporate to dryness, and we moisten the residue with a drop of ammonia.

990. It is coloured purple-red (617):

We pour upon the calculus a solution of KHO, no disengagement of ammonia.	URIC ACID.
In contact with the KHO solution ammonia is disengaged.	AMMONIC URATE.

991. It is not coloured purple-red:

The HNO_3 solution becomes *yellow* during the evaporation; the residue is insoluble in K_2CO_3.	XANTHINE.
The HNO_3 solution is coloured dark brown by the evaporation; the residue dissolves in NH_4HO, and deposits from this solution under the form of microscopic hexagonal tables.	CYSTINE.

992. The calculus is heated upon platinum foil; it takes fire and burns with a very clear white flame; it can consist of cholesterin or of fibrine.

The calculus possesses evidently a crystalline texture, it dissolves in boiling alcohol, and is deposited as the solution cools under the form of shining spangles; it is insoluble in KHO.	CHOLESTERIN.
The calculus during the combustion develops the odour of burnt horn and becomes swollen; it dissolves in KHO, from which acetic acid precipitates it; the precipitate dissolves in an excess of acetic acid, gives a solution which yields a precipitate with potassic ferrocyanide.	FIBRINE.

993. The calculus possesses a brown colour; it is friable,

ochreous, and disengages the odour of calcined animal matter in burning.

It is little soluble in alcohol and water, it dissolves in KHO which it colours dark brown; HNO_3 produces, in this solution, change of coloration characteristic of the colouring matter of the bile (933).	Colouring Matter of the Bile.
It is soluble in alcohol; the solution possesses a bitter taste; with H_2SO_4 and sugar it takes a beautiful reddish-violet colour (939).	Acids of the Bile.

994. Calculi which leave a fixed residue.—Two cases can present themselves:

A. The matter does not give, with HNO_3 and NH_4HO, the reaction of uric acid. (*See* par. 617.)

a. The residue from the calcination melts easily by heat.

The calculus does not effervesce with acids either before or after the calcination; it dissolves in HCl, NH_4HO precipitates it from this solution; $(NH_4)_2C_2O_4$ also precipitates it; heated with the blow-pipe flame, moistened with a solution of cobaltic nitrate and again heated, it furnishes a blackish-brown enamel. (See par. 198.)	Calcic Phosphate.[*]
During the calcination the calculus disengages an ammonic odour; it dissolves without effervescence in acetic acid; NH_4HO forms in this solution a cystalline precipitate. Heated with the blow-pipe flame along with a solution of cobaltic nitrate, it furnishes a dark-red glass. (See par. 198.)	Magnesic Ammonic Phosphate.

b. The residue from the calcination does not melt on being heated.

The residue is white and does not turn red litmus blue; it gives the reactions of calcic phosphate (par. 188).	Calcic Phosphate.
The original matter is not attacked by acetic acid; the mineral acids dissolve it without effervescence, and NH_4HO precipitates it from this solution; after calcination the residue possesses an alkaline reaction, and the acids then dissolve it with effervesvence (see par. 189).	Calcic Oxalate.

---

[*] Calcic phosphate, although infusible itself, becomes fusible if mixed with magnesic ammonic phosphate; the calculus produced by the mixture of these two phosphates is named, from its easy fusibility, the *fusible calculus*.

When heated by the blow-pipe flame the calculus becomes luminous; before calcination the acids dissolve it with effervescence; after the acid solution has been neutralized with NH_4HO it gives a white precipitate with ammonic oxalate.	Calcic Carbonate.

B. The matter gives with HNO_3 and NH_4HO, the reaction peculiar to uric acid (see par. 617).

a. It melts on being heated:

It communicates an intense yellow coloration to the flame.	Sodic Urate.
It does not colour the flame yellow, but violet (see par. 46).	Potassic Urate.

b. It does not melt on being heated:

The residue after calcination comports itself as calcic carbonate.	Calcic Urate.
The residue after calcination dissolves with a slight effervescence in dilute H_2SO_4; the solution neutralized by NH_4HO gives with sodic hydric phosphate a white precipitate.	Magnesic Urate.

995. When the nature of the calculus has been determined, it is always necessary to control the results by special reactions.

VEGETABLE CHEMISTRY.

996. We have given the properties and reactions of the chief members in the three following groups: Albuminoid group; the saccharine or amylaceous group, and the group of the vegetable bases.

The albuminoid group.

Albumen, Fibrin, Casein.

997. *Vegetable albumen.*—This substance exists in the juice of most vegetables, and in the solid form in certain parts of the plant, especially in the seed. It exhibits the reactions, and appears to have the same composition as animal albumen (794). "The mode of its occurrence differs, however, remarkably from that of animal albumen in this respect, that it is always found in plants in neutral or acid liquids, whereas animal albumen exists only in alkaline liquids."

998. *Vegetable fibrine, gluten.*—This substance is also found in the juices of all nutritious vegetables. When the newly expressed juice is allowed to stand for a few minutes, the fibrine it contains separates in a coagulated state, more or less impure. The juice of grasses is especially rich in this constituent, but it is most abundant in the seeds of wheat and other corn plants. It may be obtained from wheat flour by a mechanical operation, and in a state of tolerable purity; it is then called gluten. It is a soft, glutinous and elastic substance, which can be drawn out into long strings; it has scarcely any colour, taste, or smell.

999. It exhibits the same reactions, and has the same composition as animal fibrine (821).

1000. *Vegetable casein, legumine.*—This substance is found chiefly in the seeds of peas, beans, and similar leguminous seeds; hence it is frequently called *legumine.* Its composition has not been well determined, but Liebeg considers it to be identical with the caseine of milk, which it resembles in its reactions (828).

THE SACCHARINE OR AMYLACEOUS GROUP.

1001. The substances forming this group are numerous; they contain, with a few exceptions, oxygen and hydrogen, in *the proportion* to form water. The sugars and gums are the only members of the group which are soluble in cold water; starch and other similar bodies are insoluble in cold, but soluble in hot water; whilst cellulose is quite insoluble in water, whether hot or cold.

1002. We may here observe that there are three leading varieties of sugar—CANE-SUGAR (*sucrose*), GRAPE-SUGAR (*glucose*), MILK-SUGAR (*lactose*), and some chemists add a fourth, Fruit-sugar or fructose; other chemists consider it to be merely grape-sugar.

1003. We have restricted our notice of this group to the following members:—CELLULOSE, STARCH, GUM, DEXTRINE, CANE- and GRAPE-SUGARS.

CELLULOSE (*Lignin, woody fibre,* $C_6H_{10}O_5$).

1004. Cellulose forms the framework of all plants; its composition and reactions are always the same, but the properties which depend upon its state of aggregation, present the greatest differences, as its texture varies with the plant from which it is extracted. Cotton, linen, hemp, and unsized white paper, consist of cellulose very nearly pure. "The easiest method of obtaining pure cellulose, is to wash white cotton, unsized paper, old linen, or elder-pith with a hot solution of KHO or NaHO, then with cold dilute HCl, then with NH_4HO, washing thoroughly with water after the application of each of these reagents, and lastly, with alcohol and ether; it is often necessary to repeat this series of operations two or three times. To obtain pure cellulose from wood it is necessary, after boiling the wood with KHO till the liquid is almost dry, to treat it with chlorine water, or with a weak solution of chloride of lime, repeating these successive operations several times, in order to free the cellular tissue from the encrusting matter which is so intimately united with it.

1005. "Cellulose thus purified is white, translucent, of specific gravity about 1·5, insoluble in water, alcohol, ether, and oils, both fixed and volatile. When quite pure it is unalterable in the air, but as it exists in wood, in contact with azotized and other easily alterable matters, it gradually decomposes in moist air, undergoing a slow combustion, and being converted into a yellow or brown friable substance called *touchwood.*"

1006. *Dilute* acids do not act on cellulose.

1007. *Cold concentrated* H_2SO_4 disintegrates it and converts it into dextrine, a substance isomeric with cellulose, without blackening; if water be then added, and the liquid be subsequently boiled, the dextrine is converted into glucose.

1008. By immersion in strong HNO_3, or in a mixture of HNO_3 and H_2SO_4, or of KNO_3 and H_2SO_4, cellulose is converted, without dissolving or undergoing any alteration of form, into a mixture of several explosive nitrogenous compounds, called gun-cotton, or pyroxylin. More dilute HNO_3 converts it into substances allied to or identical with starch, gum, lactic acid, and malic acid; and if it is boiled with the acid for a length of time it is dissolved with complete decomposition.

1009. By immersion for a few seconds in HNO_3 of ordinary strength hemp appears *pale yellow*, flax remains *unaltered in colour*. New Zealand hemp (*Phormium tenax*) immediately becomes *blood-red;* the latter coloration is produced, even after bleaching, or after the fibre has been treated with a solution of KHO. This reaction may therefore serve for the detection of New Zealand hemp fibre in fabrics. The fibres of several plants are coloured *pale-red* by the acid. The colouring is due to the incrusting substances. Cotton is scarcely or not at all coloured by HNO_3, whereas animal fibres are coloured permanently *yellow*. This reaction may serve for the detection of cotton in woollen textures.

1010. Unsized paper, if immersed for half a minute in a mixture of ¼ to ½ volume of water and 1 volume of H_2SO_4, of ordinary strength, and immediately washed first with pure water, and then with water slightly ammoniacal, is changed into a substance called vegetable parchment. This substance can be formed from cotton as well as from flax fibres.

1011. The property of linen-fibre to acquire a deep yellow colour by boiling with a mixture of equal quantities of water and KHO, whereas cotton is little or not at all coloured by it, is applied by Böttger to the detection of linen in cotton.

1012. *Alkaline liquids* when dilute do not act upon cellulose, but when concentrated they gradually destroy its texture.

1013. "Cellulose in its natural state, is not coloured blue by iodine; but after it has been digested for a short time with H_2SO_4, it becomes of a fine blue when free iodine is added. This reaction is sometimes serviceable in the microscopic examination of vegetable tissues; cellulose being thus easily distinguished from tissues into the composition of which nitrogen enters. By the prolonged action of H_2SO_4, the property of being coloured blue by iodine disappears, the dextrine and sugar which are formed not being susceptible of the blue coloration."

1014. Cellulose dissolves completely in an ammonic solution of CuO,* forming a syrupy liquid, which may be filtered after dilution with an equal bulk of water. It is precipitated from this solution in flakes on the addition of HCl.

STARCH (*Amylum*, *Fecula*, $C_6H_{10}O_5$).

1015. This substance is deposited in grains in the cellular tissue of certain parts of plants. The form and dimension of the starch grains are tolerably uniform in the same plant, but are very variable in different species of plants.

1016. It is insoluble in *alcohol*, *ether*, and *cold water*, but when a mixture of starch and water is heated to near the boiling point, the granules burst and disappear, forming a gelatinous mass. If this paste be largely diluted with water, the swollen granules of the starch subside, whilst a certain quantity of amylaceous matter remains in solution.

1017. When dry starch is heated to about 205° C., it is converted into a substance isomeric with starch, called dextrine or British gum. This substance is soluble in cold water, forming a ropy solution much resembling gum in properties; but it differs from gum in forming a deep blue liquor in a solution of $CuSO_4$, which deposits Cu_2O when cold. It is rendered red and not blue with iodine. It has been called dextrine from its turning the plane of polarization to the *right*, when acting on polarized light.

1018. *Dilute alkalies and acids* in the cold cause starch to swell up and become partially disintegrated, but if the solution is heated it is converted into dextrine.

1019. An aqueous solution of iodine forms with starch a characteristic blue colour; this colour disappears if the iodine be added in excess, or if the solution be heated, but in the latter case, the blue colour returns as the liquid cools. Decoloration of iodide of starch or its aqueous solution is produced by all reagents which cause the iodine to enter into combination, especially by chlorine, the colour being restored by Zn and H_2SO_4; HNO_3 which converts iodine into iodic acid and destroys the starch; SO_2, H_2S, AsO_3, NH_4HO, and KHO, the blue colour when destroyed by the alkalies being restored by acids. Iodide of starch is likewise decolorized by $SbCl_3$, $AsCl_3$, $AuCl_3$, ferrous, manganous, stannous, mercurous, mercuric and argentic salts. Slightly blued starch is decolorized by fixed oils. Alcohol and ether abstract part of the iodine from iodide of starch. Infusion of galls decolorises iodide of starch; hence certain roots containing both starch and tannin are not rendered blue by iodine till after the addition of HNO_3. Decoloration is also produced by pyrogallic acid, by wood vinegar, by urine, and by tobacco vapour after the compound has been moistened with $H\bar{A}$. In presence of saliva, blood-serum, and other substances it is not produced until the liquid containing the starch has been mixed with 1—2 drops of tincture of iodine, then with a few drops of a solution of KHO, and lastly supersaturated with HNO_3.

---

* Prepared by dissolving CuO in ammonia.

GUM ($C_{12}H_{22}O_{11}$).

1020. This substance is found in the juices of almost all plants, but is met with in its purest form in transparent tears, which exude from various species of acacia. Gum-arabic may be taken as its type.

1021. The gums proper are soluble in cold water or hot; but *mucilage* or *bassorin*, a modification of gum, is insoluble in water, but when moistened with it, swells up into a gelatinous mass. Gum-arabic dried at 120° becomes insoluble in water. The gum of seeds and roots or mucilage, which appears to be a universally diffused constituent of plants, is soluble in cold water, but is insoluble in alcohol and is precipitated from its aqueous solutions by tincture of galls. Neutral lead acetate does not precipitate it completely, but the basic acetate produces complete precipitation.

1022. *Alcohol* and *ether* precipitate gum from its solution in water, in the form of white flocculi, or if dilute, in the form of a milky turbidity.

1023. Solution of KHO coagulates a solution of gum; but an excess of the reagent renders the liquid limpid.

1024. Concentrated HNO_3 converts gum into mucic and oxalic acids.

1025. If it is boiled with dilute H_2SO_4 it is transformed first into dextrin and then into glucose.

1026. If a few drops of $CuSO_4$ be added to a solution of gum mixed with KHO, a blue precipitate is produced, which is insoluble in the liquid, but which is soluble in pure water, this solution can be boiled without depositing Cu_2O. This character distinguishes natural gum from dextrine (British gum) (1017).

CANE-SUGAR or *Sucrose* ($C_{12}H_{22}O_{11}$).

1027. This variety of sugar is widely spread in the vegetable kingdom; it has been called cane-sugar because it is obtained chiefly from the sugar-cane. It has a specific gravity of 1·6. It is soluble in about one third of its weight of cold, and is much more soluble in boiling water; its solution has, as is well known, a sweet taste. Absolute alcohol dissolves about 1-80th of this sugar at its boiling point, nearly the whole of which separates in small crystals on cooling. It is more soluble in ordinary alcohol. It slowly separates from a strong watery solution in large, transparent, colourless crystals, having the figure of a modified oblique rhombic prism; if a solution of it is kept at a temperature near the boiling point it gradually loses the property of crystallizing. It melts, about 160° C., into a viscous colourless mass, which, on cooling, forms the solid known as barley sugar; if long kept this amorphous form of cane-sugar gradually loses its transparency, and becomes crystallized. If, after the sugar has melted, the application of heat be continued, until the temperature reaches 204° or 215° C. the sugar loses an equivalent of water, and a *brown, deliquescent, slightly bitter* and *unfermentiscible substance* called *caramel* remains, which is used as a colouring matter by cooks and confectioners. If the heat is continued beyond 215° C., complete decomposition ensues, inflammable gases are given off and a brilliant mass of porous charcoal remains.

1028. Cane-sugar is not rendered brown as grape-sugar is (879) on boiling it in a solution of KHO.

1029. "Concentrated H_2SO_4 acts very energetically upon cane-sugar, evolving water, carbonic and formic acids and charcoal. It is a striking experiment to mix about equal bulks of H_2SO_4 and strong syrup; the mixture, when stirred, becomes brown and black, then suddenly heats, boils up, and passes into the state of a bulky black magma:* the acid appears suddenly to abstract the elements of water from the sugar, leaving charcoal." The action of H_2SO_4 upon grape-sugar is as we have already noticed (877), very different.

1030. Strong HNO_3 converts cane and grape-sugar into oxalic acid.

1031. When cane-sugar is boiled with dilute HCl or H_2SO_4 it assimilates water and becomes converted into grape-sugar. Yeast effects the same change in its solutions. The converse change, that of converting grape-sugar into cane, has not yet been accomplished.

1032. A sugar solution has the property of dissolving many basic oxides, baryta and lime are very soluble in cold sugar solutions; when the solution of the alkaline earth is heated it becomes opaque, and when the solution reaches the boiling point the compound of sugar and the alkaline earth is deposited.

1033. If to a solution of cane-sugar a solution of caustic potash is added, and then a drop or two of a dilute solution of sulphate of copper, a deep blue liquid is obtained, which retains its *blue tint*, on being heated. This is a very good test for distinguishing the two varieties of sugar, or discovering an admixture of grape with cane-sugar (see par. 880).

---

* Cane sugar has been given as a test for free sulphuric acid in the presence of a sulphate (see par. 407).

1034. The properties of grape-sugar have already been described under animal chemistry, par. 876.

1035. Answers to the following exercises must be written out:—

EXERCISES.

180. State the method of examining a blood stain on linen, and the tests by which it is distinguished.

181. State the composition and principal properties of cellulose, describing particularly the action of strong HNO_3 upon it.

182. How would you separate hippuric acid from human urine and exhibit its characteristic properties?

183. Name the organic bodies usually present in urine, and give the methods for detecting them.

184. How would you distinguish ammonic urate from magnesic ammonic phosphate?

185. Give the composition of starch and the different kinds of sugar, and name some of their characteristic properties.

186. A deposit in urine is supposed to be uric acid. How would you ascertain whether such is the case?

187. How may urea be extracted from urine?

188. What are the tests for gelatine?

189. A deposit from urine is given you for chemical examination; what substances would you search for, and how would you conduct the examination?

190. What is the action of KHO on cupric salts, and how is this action modified in the presence of sugar?

191. What are the distinctive properties of the uric acid, xanthic acid, and cystic oxide calculi?

192. How would you analyse qualitatively a calculus composed of calcic phosphate and magnesic ammonic phosphate?

193. How is a solution of gelatine obtained, and how does it differ from one of albumen?

194. Enumerate the different varieties of urinary calculi, and explain how they may be distinguished?

195. Why does urine become ammoniacal.

196. Describe the properties of albumen and fibrine.

197. Uric acid may exist as a urinary sediment in one or other of three states. What are these, and how may they be distinguished from each other?

ORGANIC BASES AND MECONIC ACID.

1036. In this section the properties and reactions of the most important of the medicinal alkaloids and meconic acid, with reagents, are given, and the mode of extracting them in a state of purity from complicated mixtures of animal and vegetable substances; together with the more general methods of Stas and others, for the detection of poisonous alkaloids in organic mixtures.

VOLATILE ALKALOID.

NICOTINA OR NICOTINE ($C_{10}H_{14}N_2$).

1037. This alkaloid is contained in tobacco, probably in the state of malate and citrate; in its pure state it is a limpid, colourless, oily liquid; it absorbs oxygen on exposure to air, and turns brown and finally becomes solid. It has a strong and irritating odour of tobacco; is very inflammable, and burns with a smoky flame. It is miscible in all proportions with water, alcohol, and ether. It boils at 250° C., suffering, however, partial decomposition in the process; but when heated in a stream of hydrogen gas, it distils over unaltered, between 100° and 200° C. Its solutions possess an alkaline reaction. It precipitates metallic oxides from solutions of their salts, and unites with the acids, forming salts.

1038. Salts of nicotine are in general very soluble in water and alcohol, but insoluble in ether; they are difficultly crystallizable and even deliquescent.

1039. If an aqueous solution of nicotine, or a solution of a salt of nicotine mixed with a solution of NaHO or KHO, is shaken with *ether*, the nicotine is dissolved by the ether; if the latter is then allowed to evaporate on a watch-glass, the nicotine remains behind in drops and streaks; on warming the watch-glass, it volatilizes in white fumes of strong odour.

1040. *Chlorine-gas* acts powerfully upon nicotine, producing with it a blood-red liquid.

1041. Solution of I in KI and water, when added in small quantity to an aqueous solution of nicotine, produces a yellow precipitate, which after a time disappears. Upon a further addition of the iodine solution, a copious kermes-coloured precipitate separates; but this also disappears again after a time.

1042. When a glass rod moistened with HCl is brought into contact with vapour of nicotine white fumes are produced, as with ammonia. Boiled with HCl, the nicotine is coloured violet.

1043. When HNO_3 is heated with nicotine a red liquor is produced.

1044. $PtCl_4$ produces in aqueous solutions of the chloride of nicotine a yellow crystalline precipitate of chloro-platinate of nicotine, which is insoluble in alcohol and ether, slightly soluble in cold water, readily soluble in an excess of nicotine, and soluble in HCl in the cold.

1045. $AuCl_3$ produces a reddish-yellow flocculent precipitate, sparingly soluble in HCl.

1046. "If an aqueous solution of nicotine is added to a solution of $HgCl_2$ in excess, an abundant, flocculent, white precipitate is formed. If solution of NH_4Cl is now added to the mixture in sufficient quantity, the entire precipitate, or the greater part of it, redissolves. But the fluid very soon turns turbid, and deposits a heavy white precipitate.

1047. "Solution of *tannic acid* produces a copious white precipitate, which redissolves upon addition of HCl."

1048. Nicotine is extremely poisonous, a single drop of it being sufficient to kill a large dog.

1049. To extract nicotine from the animal tissues or the contents of the stomach, the animal matter is treated with a solution of KHO and then treated repeatedly with *ether* or pure *benzole*. The benzol or ether solution is evaporated at a gentle heat in a retort, the nicotine remains behind in an impure state. It is then treated with H_2SO_4, the solution, if necessary, filtered, and then treated with solution of KHO and ether or benzole as in the first instance. Nicotine may also be isolated from foreign organic matter by repeatedly exhausting the stomach, &c., with dilute acid, the acid solution is filtered and evaporated to dryness on the water bath; it is then redissolved in water and treated with KHO and ether in the manner previously described.

1050. The volatility and odour of nicotine are its most characteristic distinctions.

NON-VOLATILE ALKALOIDS.

1051. The non-volatile alkaloids are solid, and cannot be distilled over with water.

MORPHIA OR MORPHINE ($C_{17}H_{19}NO_3$).

1052. This alkaloid is contained in opium associated with narcotine and several other organic bases (see par. 1071). When crystallized from alcohol it forms small but very brilliant prismatic crystals, which are transparent and colourless; it crystallizes with an equivalent of water; at a gentle heat the water is expelled and the morphine melts and forms a tumid resinous mass which solidifies into a radiated crystalline mass. When it is obtained by precipitation it appears as a white crystalline mass. It is soluble in about 1000 times its weight of cold and in 400 of boiling water; the solution has a bitter taste. It is soluble in about 90 times its weight of cold, and from 20 to 30 parts of boiling alcohol. Its aqueous and alcoholic solutions manifest distinctly alkaline reactions. It dissolves in amyl-alcohol in the cold but more freely with the aid of heat; it is soluble in acetic ether. It dissolves according to Schlimpert in 60 parts and according to

Pettenkofer in 175 parts of chloroform. Its solubility in ether varies according to its physical condition, recently precipitated morphia dissolves in ether about three times as largely as the crystallised base; therefore, if a solution of a morphine salt has been neutralised with one of the fixed alkaline carbonates or acid carbonates ether dissolves the precipitated morphine if the ether is shaken up with the liquid at once, but not after some time, or at least to a very slight extent, as the precipitated base in time becomes crystalline, and in that condition is nearly insoluble in ether. Ether containing alcohol dissolves morphine.

1053. Acids dissolve morphine, forming with it salts which are most of them crystallizable. They are readily soluble in water and alcohol, but insoluble in ether. Its salts are exceedingly bitter to the taste.

1054. The fixed alkalies and ammonia precipitate morphine from the solution of its salts, an excess of the precipitant redissolves the precipitate. The precipitated morphine redissolves with great readiness in the fixed alkalies, but much less readily in ammonia. Lime water behaves like the fixed alkalies.

1055. The fixed alkaline carbonates precipitate morphine from the solution of its salts, and it does not redissolve in an excess of the precipitant. The fixed alkaline acid carbonates also precipitate it, and an excess does not redissolve the precipitate; these reagents fail to precipitate morphine from acid solutions in the cold.

1056. Precipitated morphine dissolves in NH_4Cl, and with difficulty in $(NH_4)_2CO_3$.

1057. If a neutral and concentrated solution of a ferric salt be added to neutral and concentrated solutions of salts of morphine, a beautiful dark-blue colour is produced, which is characteristic of morphine. The colour is not permanent and it is destroyed by an excess of acid, by the action of heat, and even by the addition of alcohol. If the solution contains an admixture of animal or vegetable extractive matters or of acetates, the colour will appear clouded or less distinct.

1058. Concentrated HNO_3 colours morphine or its salts in the solid state, and also their *concentrated* solutions orange red, which passes by degrees to yellow; this coloration is not peculiar to morphine.

1059. Iodic acid is reduced by morphine either free or combined, the liquid turning brown and emitting an odour of iodine. When solid morphine or a morphine salt is moistened with a solution of 1 part of iodic acid in 15 parts of water, and a solution of 1 part of starch in 400 parts of water is added, a *blue colour* is produced, by which $\frac{1}{300}$th of a grain may be detected: if a drop of the starch solution be previously evaporated with the morphine, the reaction will suffice for the detection of $\frac{1}{10,000}$th of a grain. If a layer of very dilute ammonia be poured upon a solution of morphine mixed with iodic acid and starch, then, even if only $\frac{1}{20,000}$th of morphine is present, two coloured rings will be formed at the surface of contact, the upper being blue, the lower brown; in more dilute solutions only the brown ring is produced. Other substances capable of reducing iodic acid may likewise produce the blue ring, but not the brown ring at the same time (A. Duprè).

1060. Dissolve morphine in strong H_2SO_4 in the proportion of 0·002 to 0·004 grain to 6 or 8 drops of the acid, then add a drop of HNO_3 whereupon, if the morphine solution has been recently prepared, a *rose-colour* is produced, changing after a few seconds to *yellow*, then to *greenish*, and finally to brown. If a small quantity of water be added to the solution of morphine in H_2SO_4, so that the mixture becomes hot, the colouring produced by the subsequent addition of HNO_3 is of a much deeper carmine red, and much more durable. If the sulphuric solution is heated for a few minutes to 100°—150°, the addition of a drop of nitric acid produces, after cooling, a splendid deep violet colour, which gradually disappears from the centre outwards, passing through blood-red. If the temperature is raised above 150° the liquid acquires of itself, at a certain moment, a violet-rose colour; at still higher temperatures, a dirty green colour is produced. On adding a drop of HNO_3, after cooling, the liquid immediately turns red, without passing through violet. A solution of morphine in H_2SO_4, left to itself for twelve to twenty-four hours at ordinary temperatures, behaves as if it had been heated to 100°—150°; as regards the sensibility of these reactions $\frac{1}{5}$ of a milligramme of morphine is sufficient to produce a very bright carmine colour; $\frac{1}{50}$ of a milligramme gives a very distinct reaction, and $\frac{1}{100}$ milligramme still gives a perceptible tint after half a minute.—(*Husemann.*)

1061. A solution of morphine in H_2SO_4, previously heated, is coloured deep red by ferric chloride, the colour changing after a time to dirty green.

1062. To detect morphine when mixed with animal matter, the substance is mixed with alumina, dried between 100° and 110°, then well pulverized and macerated in cold water acidulated with acetic acid. The solution treated with ammonia deposits morphine, which may then be recognised by its reactions with iodic acid, ferric salts, H_2SO_4, and HNO_3.

Narcotina or Narcotine ($C_{22}H_{23}NO_7$).

1063. Narcotine appears in the form of acicular groups, or in colourless, brilliant, right rhombic prisms, or when precipitated by the alkalies, as a white, loose, crystalline powder. It fuses at 171° C., solidifies again at 130° C. in the crystalline or amorphous state, according as the cooling is slow or rapid. It is insoluble in cold water, but dissolves in boiling water to the extent of 1 part in 7000. It dissolves sparingly in alcohol and ether in the cold, but somewhat more readily upon heating. Solid narcotine is tasteless, but the alcoholic and etherial solutions are intensely bitter. It dissolves in 2·6 parts of chloroform, in 60 parts of acetic ether, also in oils, both fixed and volatile. Its solutions do not possess an alkaline reaction.

1064. Narcotine dissolves readily in acids, forming with them salts, but the basic powers of narcotine are so feeble that its salts have invariably an acid reaction. "Those with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even by simple evaporation. Most of the narcotine salts are amorphous, and soluble in water, alcohol and ether; they have a bitter taste."

1065. The alkalies, and the carbonates and acid carbonates of the alkalies, precipitate narcotine immediately from a solution of its salts, in the form of a white powder, which, seen through a lens magnifying 100 times, appears an aggregate of small crystalline needles; the precipitate is insoluble in an excess of the precipitant. If a solution of narcotine is mixed with ammonia, and ether added in sufficient quantity, the narcotine which has separated upon the addition of the ammonia redissolves in the ether, and the clear fluid presents two distinct layers. If a drop of the etherial solution is evaporated on a watch-glass, the residue is seen, upon inspection through a lens magnifying a hundred times, to consist of small, distinct, elongated, and lance-shaped crystals.

1066. "*Concentrated* HNO_3 dissolves narcotine to a colourless fluid, which acquires a pure yellow tint upon the application of heat.

1067. "If the solution of a salt of narcotine is mixed with *chlorine-water*, it acqures a yellow colour, slightly inclining to green; if ammonia is then added, a much more intensely coloured yellowish-red fluid is obtained.

1068. "Narcotine added to cold H_2SO_4 colours it bluish-violet or yellow, which, if the liquid be gently heated, changes to orange-red, then to violet-blue at the edge of the dish, and lastly violet-red. This reaction is very distinct, if the H_2SO_4 contains 1 part in 2000 of narcotine; and even if it contains only 1 part in 40,000, a slight carmine colour is still perceptible, passing into violet-red."—*Husemann.*

1069. A solution of narcotine in cold H_2SO_4 becomes reddish-yellow on addition of HNO_3; with hypochlorite of soda the same colour is produced, but preceded by a carmine tint. If the solution has been heated, both reagents immediately produce a light yellow colour, becoming slightly reddish after a while.

1070. A solution of narcotine in H_2SO_4, previously heated, acquires, on addition of ferric chloride, a dark red colour, changing to cherry-red, which lasts twenty-four hours.

1071. Opium contains, besides morphine and narcotine, the following crystallizable alkaloids—*codeine*, *thebaine*, *narceine*, and *papaverine*. The following table shows the difference in the solubility of these alkalies in different liquids:

	Water.	Alcohol.	Ether.	Potash.
Morphine . .	Slightly soluble	Easily soluble	Almost insoluble	Soluble in an excess
Narcotine . .	Almost insoluble	Soluble	Soluble	Insoluble
Narceine . .	Slightly soluble	Soluble	Insoluble	Soluble in weak potash
Codeine . . .	Soluble	Extremely soluble	Extremely soluble	Insoluble in concentrated potash.
Thebaine . .	Insoluble	Soluble	Soluble	Soluble in weak potash.
Papaverine . .	Insoluble	Soluble	Soluble	Insoluble.

QUINA OR QUININE ($C_{20}H_{24}N_2O_2$).

1072. This alkaloid exists in combination with kinic acid in cinchona barks; it forms two hydrates, containing respectively 1 and 3 atoms of water; the latter is the ordinary hydrate. It appears either in the form of silky needles, or as a loose white powder. It melts at 120° C., and gives up its water of crystallization. It requires about 350 parts of cold water and 200 of boiling water for its solution. It is readily soluble in alcohol, both hot and cold; it is less soluble in ether; it dissolves in 60 parts of the latter liquid. It is also soluble in chloroform and the essential and fixed oils. Its solutions have an alkaline reaction and are intensely bitter.

1073. Acids dissolve quinine, forming with it salts which are crystallizable, and difficultly soluble in cold, but readily soluble in hot water and in spirit of wine. The acid salts dissolve very freely in water; the solutions exhibit the remarkable phenomenon of *fluorescence* or *epipolic dispersion*—a magnificent blue luminosity seen upon the surface of the liquid when viewed in reflected light, and which is owing to a change effected in the *actinic* rays by the dissolved quinine salt. The salts of this base are intensely bitter.

1074. The fixed alkalies, ammonia, and the alkaline carbonates precipitate quinine as trihydrate from a solution of its salts in an amorphous state, which after some time becomes crystalline. The precipitate is only soluble in the fixed alkalies to a barely perceptible extent; but it is more soluble in ammonia. In the solutions of the fixed alkaline carbonates, it dissolves to about the same extent as in pure water.

1075. "The addition of *chlorine-water* to the solution of a salt of quinine fails to impart a colour to the fluid, or at least imparts to it only a very faint tint; but if ammonia is now added, the fluid acquires an intense emerald-green colour; by this reaction, especially by employing an etherial solution, mere traces of quinine may be recognised; quinidine, however, exhibits the same reaction. If, after the addition of the chlorine water, some solution of potassic *ferrocyanide* is added, then a few drops of *ammonia* or some other alkali, the fluid acquires a magnificent deep red tint, which, however, speedily changes to a dirty brown. This reaction is delicate and characteristic. Upon addition of an acid (acetic acid answers the purpose best) to the red fluid, the colour vanishes, but reappears afterwards upon cautious addition of ammonia.

1076. As cinchonine and quinidine exist together with quinine in cinchona-barks, their sulphates may occur as impurities in sulphate of quinine; they may be recognised by the following *quinine test* of Liebeg:—10 grains of the sulphate to be tested are warmed with 10 drops of dilute H_2SO_4, and 15 drops of water in a test tube, the solution is allowed to cool, and then 60 drops of commercial ether and 20 drops of ammonia-water are added, and the whole is shaken and the tube stopped. If the quinine were free from cinchonine, and did not contain more than 10 per cent. of quinidine, the whole remains in solution; but if cinchonine were present, it is deposited as a white pulverulent layer between the ether and the water, as is also the case with quinidine when present in large quantity. Smaller portions of quinidine crystallize from the ether on standing for a short time, and still smaller quantities when ether saturated with quinidine is employed in the first instance. As it sometimes happens that the upper etherial layer solidifies to a jelly, even with pure sulphate of quinine, it is more convenient to employ ether containing alcohol, or to take a somewhat larger proportion of ether than is directed above.—*Gmelin.*

1077. Stoddart has proposed the following modification of Liebig's process:—Into a glass tube or bottle put 10 grains of the suspected salt, dissolve in 10 minims of dilute H_2SO_4 and 60 minims of distilled water; to this add 150 minims of pure ether, 3 minims of alcohol, and 40 minims of a solution of soda (1 part of solid NaHO to 12 of water). Agitate well and set aside for twelve hours, when, if the slightest trace of quinidine or cinchonine be present, they will be seen at the line of separation between the ether and solution of Na_2SO_4. If only a small per-centage of quinidine be present, it will appear as an oily substratum, appearing under a lens as dust, from the minuteness of its particles. Cinchonine will appear more decidedly crystalline. With a little practice the eye will easily distinguish which of the alkaloids is deposited.

CINCHONINE ($C_{20}H_{24}N_2O$).

1078. This alkaloid exists, together with quinine, in most of the true cinchona barks; it appears either in the form of transparent brilliant, four-sided prisms, or fine, white, crystalline needles, or, if precipitated from concentrated solutions, as a loose white powder; in its crystalline state it is anhydrous. It is nearly insoluble in cold water, and requires for solution 2500 parts of boiling water. It is less soluble in alcohol than quinine, and is more soluble in hot than cold alcohol. The greater portion of the cinchonine dissolved by hot alcohol, separates in a crystalline form as the solution cools. It dissolves in 470 parts of boiling ether and 23·2 parts of chloroform. Solutions of cinchonine have an alkaline reaction and a bitter taste. It fuses at 165° C., to a colourless liquid, which becomes a crystalline mass on cooling.

1079. The acids dissolve cinchonine, forming with it salts which are most of them crystallizable; they are soluble in water and alcohol, insoluble in ether. They are exceedingly bitter to the taste.

1080. The fixed alkalies, ammonia, and the neutral alkaline carbonates precipitate cinchonine from a solution of its salts, in an amorphous state, an excess of the precipitant does not redissolve the precipitate.

1081. "If the solution of a salt of cinchonine containing only very little or no free acid, is mixed with potassic ferrocyanide, a flocculent precipitate of ferrocyanide of cinchonine is formed. If an excess of the precipitant is added, and a gentle heat very slowly applied, the precipitate dissolves, but separates again upon cooling, in brilliant gold-yellow scales, or in long heedles, often aggregated in the shape of a fan. With the aid of the microscope, this reaction is as delicate as it is characteristic."

STRYCHNINE ($C_{21}H_{22}N_2O_2$).

1082. This alkaloid exists, together with brucine and igasurine, in nux vomica, in St. Ignatius' beans, in the strychnos colubrina, and several other varieties of strychnos; it crystallizes from dilute alcohol, in white anhydrous octohedra, or in square prisms, which do not fuse on the application of heat; when it is produced by precipitation or rapid evaporation, it appears as a white powder. Cold water does not dissolve more of it than $\frac{1}{7000}$th of its weight, and it is only slightly more soluble in hot water. It is only sparingly soluble in dilute alcohol, and almost insoluble in absolute alcohol and ether. It dissolves freely in amyl-alcohol, and is soluble in chloroform and the essential oils. It is very bitter to the taste; even when its cold aqueous solution is diluted with 100 times its weight of water, it still possesses a distinctly bitter taste.

1083. Acids dissolve strychnine, forming with it salts, most of which are crystallizable; they are soluble in water, and are very bitter to the taste.

1084. The fixed alkalies and their carbonates precipitate strychnine from solutions of its salts. The precipitate is insoluble in an excess of these reagents; and the strychnine is only precipitated after the lapse of some time from dilute solutions.

1085. Ammonia precipitates strychnine from a solution of its salts, but the precipitate is soluble in an excess of the ammonia, from which solution the strychnine separates after some time, in the form of needles; the length of time required for the separation depending upon the strength of the solution.

1086. If strychnine is dissolved in a drop or two of *pure* concentrated H_2SO_4 (the acid must be free from nitrous acid), it forms a colourless solution, which yields coloured reactions with most oxidizing substances; the oxidizing substances are added in the solid form, and in small quantities. The following reagents give the colorations named, with the sulphuric solution of strychnine:—*a. Peroxide of lead* gives a blue coloration, becoming violet, then red, and finally, in a few hours, yellow. *b. Acid potassic chromate* gives a fine violet coloration; if the quantity of strychnine present is large, the colour is pale blue. *c. Potassic ferrocyanide* yields a somewhat similar reaction to *b*, but more permanent. *d. Black oxide of manganese* affords a violet coloration, becoming dark red in the course of an hour. The presence of santonin, or starch, does not prevent the recognition of strychnine by acid potassic chromate in the above solution; sugar, quinine, or morphine renders it indistinct, but does not affect the reaction with peroxide of lead. The presence of thirty parts of tartar emetic does not prevent the coloration with acid potassic chromate, but sixty parts render it indistinct. Very small quantities of animal or vegetable extractive matters render the above reactions indistinct, where the strychnine is present in minute traces only. It is, therefore, always advisable to free the strychnine first, as far as practicable, from all foreign matters before proceeding to try any of these colour tests; methods for freeing it from organic matter are given in pars. 1089, 1090, and 1091. *These, and similar colour experiments, ought to be performed on a piece of white porcelain.*

1087. Concentrated HNO_3 dissolves strychnine, forming a solution colourless in the cold, but which becomes slightly yellow on heating if the strychnine is pure.* If to this solution a small quantity of peroxide of lead be added, the same changes of colour may be witnessed as in the preceding experiment.

1088. "Strychnine is associated in nature with the next base, brucine, which may be readily distinguished from it by being soluble in absolute alcohol. The action, too, of nitric acid upon the two bodies differs; it dissolves brucine and colours the solution intensely red; when heated, this colour changes to yellow; and if $SnCl_2$ or $(NH_4)_2S$ be then added, the colour again changes and becomes a most intense violet."

1089. *Detection of Strychnine in the presence of Animal Matter.*—The mixture to be examined, which, if solid, should be cut into small pieces, must be digested in dilute HCl (one part of strong acid with ten parts of water) at a temperature of 60° to 80° C. The liquid is strained and the residue is again exhausted with hot water containing HCl. The extracts are then mixed with a slight excess of ammonia, and evaporated to dryness on the water-bath, together with some clean sand. The dry residue is exhausted three or four times with hot amyl-alcohol, and these alcoholic solutions are filtered through paper moistened with *the* alcohol. The filtrate contains, besides strychnine, fat and colouring matter, which are got rid of by shaking the filtrate with ten or twelve times its volume of hot water containing HCl; the strychnine is dissolved in the acidulated water, whilst the greater part of the fat and colouring matter remains in the amylic alcohol. The hot acid solution must be shaken with fresh portions of *the* alcohol, so long as the alcohol continues to dissolve fat and colouring matter; after this the acid solution, mixed with a *slight* excess of ammonia, is evaporated on the water-bath, and the residue again exhausted with hot amylic alcohol, which dissolves the free strychnine and leaves it behind on evaporation. If the strychnine should not be sufficiently pure, it is again dissolved in dilute HCl, shaken with amyl-alcohol, and the process continued as before. When pure, it may be recognised as directed at par. 1086.

---

* If brucine is present in the strychnine, which is the case with most commercial specimens, the colour produced by the HNO_3 is deep orange or red (see par. 1088).

1090. " The presence of strychnine may be detected in very minute quantities in complicated *organic liquids*, by rendering them alkaline with a solution of KHO, and agitating thoroughly with a few drachms of chloroform; the chloroform dissolves the strychnine, and leaves it in the solid form on evaporation. From this residue it may be extracted by dilute HCl, and may afterwards be submitted to the usual tests."

1091. To detect strychnine in *beer*, shake the beer with animal charcoal in the proportion of four ounces of charcoal to a gallon; let it stand over night, collect and wash the charcoal once or twice with cold water, and boil it for half an hour with eight ounces of alcohol, which takes up the strychnine. The residue which remains on evaporating the alcohol is shaken with a few drops of KHO and ether, the latter of which takes up the strychnine. The alkaloid may be recognised after evaporating the etherial solution, by means of H_2SO_4 and acid chromate of potash.—*Graham and Hofmann.*

BRUCINE ($C_{23}H_{26}N_2O_4$).

1092. In addition to the sources of this alkaloid named in par. 1082, it exists in large quantity, unaccompanied by strychnine, in false angustura bark. It appears either in the form of transparent oblique rhombic prisms, or in that of crystalline needles. It melts readily on the application of heat, and loses its water of crystallization. It is easily distinguished from strychnine, which it resembles in many respects, by its ready solubility, both in dilute and absolute alcohol. It is difficultly soluble in cold, but somewhat more soluble in hot water; one part dissolving in about 850 parts of cold and 500 parts of boiling water. It is soluble in amyl-alcohol. It is insoluble in ether and fixed oils. Its taste is intensely bitter.

1093. The acids dissolve brucine, forming salts, most of which are crystallizable; they are readily soluble in water, and are very bitter to the taste.

1094. The fixed alkalies and their carbonates precipitate brucine from a solution of its salts; the precipitate is not soluble in an excess of these reagents. "Viewed under the microscope immediately after precipitation it appears to consist of very minute grains; but upon further inspection these grains are seen—with absorption of water—to suddenly form into needles, which latter subsequently arrange themselves, without exception, into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye."

1095. Ammonia precipitates brucine from its solutions; the precipitate appears at first in the form of minute drops of oil, but which finally change to white needles. The precipitate is very soluble in an excess of ammonia; but it is deposited after a time, the length of time depending upon the strength of the solution, from the ammoniacal solution in a crystalline state.

1096. The nitric acid reaction described in par. 1088 is characteristic for brucine.

MECONIC ACID ($C_7HO_7H_3$).

1097. This acid is one of the constituents of opium; it crystallizes in micaceous scales, or small rhombic prisms, containing 3 atoms of water, which it gives off at 100° C., leaving a white, opaque, effloresced mass. It has a sour taste, and reddens litmus strongly. It dissolves readily in water and alcohol, less easily in ether.

1098. It is easily oxidized by HNO_3, and it is also decomposed on being boiled in a strong solution of KHO.

1099. Ferric chloride imparts to solutions of the acid and its salts a blood-red colour, which is distinguished from ferric acetate by not altering in colour by boiling, and from ferric sulphocyanide by not being bleached by treatment with corrosive sublimate.

1100. Plumbic acetate precipitates the acid from its solutions as plumbic meconate; this lead salt is decomposed by H_2S, PbS being formed, and meconic acid set free.

Detection of opium in organic mixtures, tissues, &c.

1101. If the suspected substance *is a solid* it should be cut into small pieces; if it is *not in the solid state* it should be evaporated nearly to dryness on the water-bath. The original solid, or the solid obtained by evaporation, must be digested in a small quantity of water containing a little acetic acid either in a flask or dish on the water-bath for an hour or so; the mixture is then filtered, and to the filtrate, which must still contain a slight excess of acetic acid, is to be added plumbic acetate as long as any precipitate is produced; the meconic acid, if present, will be precipitated (par. 1100), whilst the morphia will remain in solution in combination with acetic acid. The mixture must be warmed, but not boiled, and afterwards allowed to cool. When cold it is filtered, the filtrate is examined according to 1103, and the precipitate according to 1102.

1102. The precipitate having been thoroughly washed with water, is removed into a beaker and mixed with water; a current of H_2S is then passed through the mixture, which is occasionally stirred during the passage of the gas; when the gas is in excess the mixture is filtered; the filtrate contains the meconic acid, the precipitate consisting of PbS. The filtrate is warmed and, if necessary, concentrated at a temperature not exceeding 71° C., to expel the H_2S. It is then tested for meconic acid as directed at par. 1099.

1103. To the filtrate from the acetate of lead precipitate, and which will contain the morphia if present, is added H_2S

in excess to precipitate the excess of Pb which was added; when the gas is in excess the mixture is filtered, and the filtrate which contains the morphia as acetate is evaporated to a small bulk on the water-bath. To the concentrated solution is added potassic carbonate slightly in excess, which precipitates the morphine; the mixture is then agitated with an etherial solution of acetic ether. After subsidence the etherial solution is poured off and allowed to evaporate spontaneously, when there is left a residue of morphia in more or less well-defined crystals, to which the tests 1059, 1060, can be successfully applied.

Methods for the detection of poisonous alkaloids in organic mixtures.

1104. When the organic bases have to be sought for among the *contents* of the stomach or intestines, or in *articles of food*, or in *pappy matters*, the substances to be examined are treated with twice their weight of pure absolute alcohol, to which from ten to thirty grains of tartaric or oxalic acid, in preference tartaric acid, have been added, and the mixture is heated in a flask or retort to between 70° and 75° C. When quite cold the mixture is filtered and the insoluble portion is washed with strong alcohol, the washings being collected with the filtrate. The filtered liquid is evaporated in vacuo, or in a tubulated retort, through which a strong current of air is passed at a temperature of not more than 33° C. If after the volatilization of the alcohol, the liquid residue contains fatty or other insoluble matters, it must be again filtered, the filter being moistened with water, and the filtrate and the washings of the residue on the filter evaporated under an air-pump or under a bell-jar over concentrated H_2SO_4 until nearly dry. The residue is then treated with cold absolute alcohol, taking care to exhaust the substance thoroughly; this alcohol solution is left to evaporate in the open air at the ordinary temperature, or still better in vacuo; this residue we will name *a*.

1105. *Solid matter*, such as the lungs, liver, heart, &c., must be cut into very small pieces, then moistened with absolute alcohol acidified with tartaric or oxalic acid as in the preceding par.; after pressing out the liquid this treatment with alcohol must be repeated *until all the soluble matter is completely extracted.* Collect the fluids obtained, and filter and allow the filtrate to evaporate in the open air at the ordinary temperature or better still in vacuo; this residue we will name *b*.

1106. The *a* or *b* residue must be dissolved in the smallest possible quantity of water, and pure acid carbonate of soda or potash *in powder* must be added gradually to the solution until it is neutralized. The neutralized solution must be *immediately* shaken with four or five times its volume of *pure* ether to dissolve the alkaloid; it must be allowed to settle, and when the layer of ether has become perfectly clear, a little of it is removed into a watch-glass, and allowed to evaporate spontaneously. If after the evaporation of the ether oily streaks remain upon the glass and gradually collect together at the bottom of it, a *liquid and volatile* alkaloid is probably present. If this be the case, the warmth of the hand will be sufficient to cause the contents of the watch-glass to exhale a disagreeable smell, which, according to the nature of the alkaloid, is more or less sharp, choking and irritating. *When a volatile alkaloid is indicated,* examine the ether solution according to par. 1109.

1107. If the residue left in the watch-glass on the evaporation of the ether is a *solid*, or a *turbid fluid* with *solid particles* suspended in it, a *solid non-volatile alkaloid is indicated;* in this case the warmth of the hand may cause the residue to emit a disagreeable animal smell, but not a pungent odour. When a non-volatile alkaloid is indicated, examine the ether solution according to par. 1111.

1108. Stass's process is given for the purification when a volatile alkaloid has been indicated, and Otto's modification of Stass's method when a non-volatile alkaloid is suspected.

1109. *A volatile alkaloid has been indicated in the trial sample.* To the solution from which the trial sample of ether was taken, add one or two cubic centimètres of a strong solution of KHO or NaHO; shake the mixture, then let it rest until the ether solution has separated perfectly from the alkaline one; then remove the etherial (supernatant) fluid into a flask, and treat the alkaline solution with a fresh portion of ether as before; draw off the ether solution into the flask which contains the former ether fluid, and repeat the treatment of the alkaline fluid with ether two or three times more, the ether solutions so obtained being all mixed together; the mixture is then to be shaken with 1 or 2 cubic centimetres of a mixture of 4 parts by weight of water and 1 part by weight of H_2SO_4; after being allowed to stand, the ether is drawn off, and the acid liquid is washed with a second quantity of ether. As the sulphates of the volatile alkaloids are soluble in water, and as almost all of them are insoluble in ether, the alkaloid sought is contained in the acid solution in the form of pure sulphate.* The ether, on the other hand, retains all the foreign organic matter which it has dissolved out from the alkaline solution. The ether solution leaves, therefore, upon spontaneous evaporation, a trifling faint yellow residue, of a nauseous odour, and containing a small quantity of conine sulphate, if that base were present.

1110. *Mix the acid solution* (which will contain one or all of the following bases if they are present, as their sulphates are entirely insoluble in ether—sulphates of ammonia, nicotine, aniline, picoline, and petinine; and the solution will also contain the greater part of the conine, if that base is present) with a concentrated solution of NaHO or KHO in excess, then agitate and exhaust the mixture with pure ether, which will dissolve the liberated bases, including ammonia; the ether solution is drawn off, and then allowed to evaporate at as low a temperature as possible;† almost all the ammonia volatilizes with the ether, whilst the alkaloid remains as residue. To eliminate the last traces of ammonia, the vessel containing the alkaloid is placed for a few minutes in a vacuum over H_2SO_4; the alkaloid then remains in a state of purity, and the analyst must determine by appropriate tests what alkaloid it is.

---

* Sulphate of conine is not quite insoluble in ether, a little of this alkaloid will therefore remain in the ether solution; the greater part, however, will remain in the aqueous acid solution.

† If conine be present some of it will evaporate with the ether.

1111. *A non-volatile alkaloid has been indicated in the trial sample.* Let the etherial solution from which the trial sample was taken evaporate spontaneously, dissolve the residuary impure alkaloid in a little water containing some H_2SO_4, and then shake the solution repeatedly with ether, which will dissolve the foreign matters present, and will not dissolve the sulphates of the alkaloids. Remove the ether solution, and then add to the *aqueous acid solution* Na_2CO_3 in excess, and then add some ether immediately and shake repeatedly (the ether dissolves the liberated alkaloid); draw off the ether solution and let it evaporate, when the alkaloids which were held in solution by the ether will be left in a very pure state, and, to a great extent, in the crystalline form; the analyst must now determine by appropriate tests what alkaloid is present.

1112. Uslar and Erdmann employ, instead of absolute alcohol and oxalic or tartaric acid, HCl and amyl alcohol in the manner described at par. 1104.

1113. *Dialytic method.*—The dialytic method devised by Graham, and noticed at par. 269, may also be advantageously employed to effect the separation of alkaloids from the contents of the stomach, intestines, &c. Acidify with HCl, and place the matter in the dialyser. The alkaloids, being crystalline bodies, dialyse into the outer fluid for the greater part in about twenty-four hours; from this solution they may, then, according to circumstances, either be thrown down at once, after concentration by evaporation, or they may be purified according to the general method just given.

1114. Answers to the following exercises must be written out.

EXERCISES.

199. Specify the colour-tests for morphia, strychnia, and quinine.

200. Name the alkaloids in nux vomica, and describe their characteristic reactions.

201. How is iodic acid employed as a test for morphia?

202. How would you examine the contents of a stomach for strychnine? What sort of evidence would you consider necessary to place the presence of the alkaloid beyond doubt?

203. How is morphia detected in organic mixtures?

204. Describe the processes required for the identification of nicotine.

205. Give the tests by which quinine, cinchonine, and quinidine, are distinguished from each other, particularising the simplest and most certain.

206. Give an account of the preparation and leading properties of meconic acid.

207. What are the distinguishing properties of meconic acid and morphia?

PART III.

OPERATIONS.

SOLUTION.

1115. Many solid bodies, when placed in contact with a liquid, possess the property of becoming thoroughly incorporated with it, by passing into the fluid state. This change is expressed by the term *solution*, and the liquid in which the solid dissolves is called the *solvent*.

1116. Solutions are of two kinds, *simple* and *chemical*. A *simple* or *mechanical solution* is the mere dissolving of a solid in a liquid, no chemical change occurring in either; on the removal, therefore, of the liquid by evaporation, the solid is obtained in its original condition. Common salt dissolved in water affords an illustration of a simple solution.

1117. In a *chemical* solution the solid and fluid combine together, forming an entirely new substance, from which the original solid and fluid can no longer be extracted by mere mechanical operations. Chalk dissolved in HCl affords an example of a chemical solution.

1118. The solvent in a simple solution cannot dissolve unlimited quantities of the substance to be dissolved; it can only dissolve certain fixed quantities of the solid, the amount varying with the kind of solid, and the amount of any particular solid varying with the solvent. When the solution contains as great a quantity of the solid matter as it is capable of disolving, it is said to be *saturated*. A solution is known to be saturated when fresh solid matter of the same sort, on being put into it, remains undissolved. But as fluids dissolve generally larger quantities of a substance the higher their temperature, the term *saturated,* as applied to simple solutions, is only relative, and refers invariably to a certain temperature. From the tendency of heat to diminish the force of cohesion, it naturally results that the solubility of most bodies is increased by heat; this, however, is not always the case; some bodies, as common salt, are equally soluble in water at all temperatures, whilst, in other cases, the solubility is greater at particular temperatures than either above or below them. The liquids employed as solvents in simple solutions are water, alcohol, ether, oils, &c. The most important solvent is water; the others are only resorted to when the substance to be dissolved is insoluble in that liquid.

1119. "A chemical solution may be *accelerated* by elevation of temperature; and this is, indeed, usually the case, since heat generally promotes the action of bodies upon each other. But the *quantity* of the dissolved body remains always the same in proportion to a given quantity of the solvent, whatever may be the difference in temperature—the combining proportions of substances being invariable, and altogether independent of the gradations of temperature." The liquids which produce chemical solutions are, in most cases, either acids or alkalies.

1120. The process of solution is conducted either in evaporating dishes or test-tubes. The latter are generally employed when the quantity of the solid operated upon is small. The more minutely any substance is powdered, the more its solution is facilitated. Solid substances are generally reduced to powder in mortars.

PRECIPITATION.

1121. It is frequently necessary to remove a constituent—it may be either the metal or metalloid of some binary compound, or the acid or base of some ternary one—from the liquid in which the compound is dissolved. This is effected by making it a constituent of some new compound, which is insoluble in the liquid in which the original compound was dissolved. This operation, which is called precipitation, is owing, therefore, to the formation of a new solid substance, which is insoluble in the liquid in which its constituents were dissolved, and which falls, or is precipitated to the bottom, owing to the solid being specifically heavier than the liquid. Occasionally, however, it is lighter, and floats upon the surface. In both cases, the insoluble substance is called the *precipitate*, and the substance producing the precipitation is termed the *precipitant.*

1122. Precipitation is an operation which is constantly practised in the preparation of substances in the manufactory as well as in the laboratory. We also resort to it in the laboratory for the purposes of detecting and separating substances one from another. Thus, if we had a solution which might contain some compound of Ba and Ca: to ascertain whether Ba was present, and, if it was, to separate it from the solution, before ascertaining whether Ca was likewise present, we might add a soluble chromate; if Ba was present, $BaCrO_4$ would precipitate, being insoluble in water, whilst $CaCrO_4$ being soluble, would remain in solution. If we were now to add to the clear, filtered solution, some soluble oxalate, CaC_2O_4, being insoluble in water, would precipitate. If the chromate produced no precipitate, there could be no Ba; if the oxalate produced no precipitate, after having separated the Ba (if present), Ca must be absent.

1123. Precipitates are classified, according to their appearances, into *crystalline*, *pulverulent*, *flocculent*, *curdy*, and *gelatinous*. The terms *turbid* and *turbidity* are applied when the precipitate is so small that it cannot be distinguished, except by impairing the transparency of the fluid.

1124. The separation of precipitates from liquids is, with some few exceptional cases, much assisted by the application of heat and agitation. The operation, when performed as an analytical operation, is conducted in test-tubes, which, from their transparency, admit of an inspection of the process.

FILTRATION AND DECANTATION.

1125. These terms are applied to a modification of the same operation—viz., the mechanical separation of fluids from solid matter mixed with them.

FILTRATION.

1126. In filtration, the separation of the fluid from the solid matter is accomplished by passing it through filtering paper of a proper size and shape, supported in a funnel. The pores of the paper permit the fluid to pass through; whilst the solid matter, being prevented, remains behind.

1127. To prepare a filter, take a small piece of filtering paper (the best white blotting paper), and fold it twice, from side to side; then round off with scissors the projecting corners, so that the paper may fall wholly within the funnel; moisten the paper when placed within the funnel, and then carefully pour the liquid to be filtered upon it. The funnel, when large quantities have to be filtered, is supported in one of the rings of the retort stand; but in the ordinary filtrations required in qualitative analysis, it may rest on the mouth of a test-tube. The filter should not project over the edge of the funnel, especially if the substance in the filter requires to be washed. Should the first portions of the liquid which pass through the filter not be perfectly bright, which is frequently the case, they must be returned to the filter, and this must be repeated until it is perfectly bright. The liquid which passes through the filter is called the *filtrate.*

DECANTATION.

1128. When the solid particles are very heavy, the supernatant liquid can be perfectly separated, without passing it through a filter, by simply inclining the vessel, so as to allow the fluid to pass away unattended by the precipitate, or by removing the fluid by a syphon.

1129. The separation in this way of a solid from a fluid is called *decantation.*

1130. Too great attention cannot be paid to the washing of precipitates when they are required for further examination. After the precipitate has been thrown upon the filter, a stream of water must be projected from the wash-bottle upon it, from time to time, until it is perfectly freed from *soluble matter;* this is soon accomplished if hot water be employed. Hot water may therefore be used in all cases unless the contrary be expressly stated.

EVAPORATION.

1131. This process is used for the purpose of obtaining matter in a solid state from solutions. By the aid of heat, the volatile fluid passes off in the gaseous form, whilst the non-volatile matter remains behind.

1132. If the evaporation be conducted slowly, the solid matter will frequently, on being deposited, assume a crystalline form. The operation is then termed *crystallization.*

1133. This operation is frequently conducted for the purpose of obtaining a liquid in a more concentrated form, by volatilizing a portion only of the fluid. Vessels are constructed expressly for the purpose called evaporating dishes.

DISTILLATION.

1134. This operation, like the former one, consists in the separation of a *volatile* from a *less volatile* fluid, or in the separation of a *liquid* from a *solid.* But in evaporation no attention is paid to the volatilized fluid, whilst in distillation it is frequently the only substance required. A distilling apparatus is therefore so constructed as to allow the evaporated fluid to be collected, which is called the *distillate.* It consists of three parts :—1. A vessel in which the liquid to be distilled is heated. 2. An apparatus in which the vapour is cooled and condensed. 3. A vessel for receiving the distillate.

1135. On a small scale, glass retorts are employed; but in the distillation of large quantities, the stills are usually made of metal.

IGNITION.

1136. By this operation volatile is separated from non-volatile solid matter; it requires the application of a high temperature, and must be conducted in crucibles. This process is therefore an *evaporation of solid bodies.*

SUBLIMATION.

1137. By sublimation we effect not only the separation of volatile from less volatile solid matter, but by cooling we bring the volatile matter back to the solid state, and in this state it is called the *sublimate.*

1138. This process is therefore a *distillation of solid bodies.*

FUSION.

1139. This term is applied to the liquefaction of a solid, by the mere application of heat. It is also used for the decomposition of solids in the "dry way."

1140. By this operation we are able to resolve insoluble substances into forms which admit of solution. This is accomplished by causing their proximate elements to unite with bodies the compounds of which will be capable of solution. Thus $BaSO_4$, which, from its insolubility both in water and acids, resists the action of reagents in the fluid state, is decomposed in this way. It is mixed with three or four times its own weight of dry Na_2CO_3, and the mixed mass exposed in a crucible for some time to a high temperature. The two salts mutually suffer decomposition when placed in these conditions, $BaCO_3$ and Na_2SO_4 being formed. If the fused mass be treated with water, the Na_2SO_4 dissolves in that liquid, whilst the Ba_2CO_3, being insoluble, remains undissolved, and, after being well washed, may be dissolved in HCl or HNO_3. The fusion takes place at a lower temperature if a mixture of equal parts of Na_2CO_3 and K_2CO_3 are employed, than if either of the carbonates were used separately.

DEFLAGRATION.

1141. This term is applied to all decompositions attended with noise. It also includes the oxidation of a substance by a reagent, in the dry way, on account of the slight explosions which frequently attend this kind of oxidation.

THE BLOWPIPE.

1142. The mouth blowpipe is a small instrument which is employed for directing a fine and continuous stream of air into the flame of a candle or lamp. By the flame thus produced two reverse chemical operations may be performed, viz., *oxidation* and *reduction*. The flame is therefore distinguished by these properties into the outer or *oxidizing* flame and the inner or *reducing* flame.

1143. In the *oxidizing* flame, the inflammable vapour is in a state of complete combustion, being supplied and mixed with an excess of atmospheric air. From the high temperature resulting from the perfect combustion of the inflammable vapour, and likewise from the excess of oxygen, all the requisite conditions are present for causing substances with an affinity for that element to enter into union with it.

1144. In the *reducing* or *deoxidizing* flame the inflammable vapour is in an incomplete state of combustion, due to a deficiency of atmospheric air; hence any metallic oxide placed in this portion of the flame is robbed of its oxygen by the inflammable vapour, which requires that element for its combustion.

1145. A *reducing flame is obtained* by keeping the nozzle of the blowpipe in an inclined direction, parallel to the surface of the wick, and just touching the exterior surface of the flame. An *oxidizing flame is obtained* by keeping the nozzle of the blowpipe at the same inclination as in the former case, and introducing it into the flame to about one third the breadth of the wick, at such a distance only from the surface of the latter as to obtain a clear, unbroken flame. A weak blast of air is only required for the reducing flame, but a strong blast is required for the oxidizing flame.

1146. The *colour* of the reducing flame is *bright yellow* if an oil lamp or candle is used; but if gas is used, it should be of the same blue colour as the centre of the oxidizing flame. The colour of the oxidizing flame in all cases is a pale-blue, almost invisible by daylight.

1147. "When any substance is submitted to the action of the *reducing flame*, it should be so held as to be entirely surrounded by the reducing flame, and protected from the oxidizing action of the surrounding atmosphere; but this condition being fulfilled, it should be held as near as possible to the point of the flame, in order to gain the greatest amount of heat and prevent any deposition of soot, which would shield the substance from the action of the flame, and would be occasionally attended with other disadvantages."

1148. When a substance is submitted to the action of the *oxidizing flame*, it should be held just beyond the point of this flame if a candle or oil lamp is used; but if gas is used, it should be held at a considerable distance (viz., one half to three quarters of an inch) beyond the point of the visible flame.

1149. "As the current of air which is supplied ought to be continuous, its production requires some attention and address. The air is not blown directly from the lungs, but is forced from the mouth by means of the cheeks. The difficulty consists in inspiring and expiring through the nose, while a continued stream escapes from the mouth. This may be attained by attention to the following directions:—Inflate the mouth fully, and then, with the lips firmly closed, and the back of the mouth closed by the tongue, breathe freely through the nostrils. While the respiration proceeds, and the mouth is inflated, allow a little air to escape through a very minute opening between the lips, renewing the supply in the mouth by occasionally admitting air from the lungs without interfering with the process of respiration through the nose."—*Parnell.* In attempting this, the student will not, probably, be immediately successful, but a few days' persevering practice will enable him entirely to master this primary difficulty.

1150. *The flame of the blowpipe.*—When coal-gas is available, it is to be preferred, since it is perfectly free from dirt and grease, and admits of being regulated with the greatest nicety. The gasburner ought to be of an oblong shape instead of round, the current of air being blown lengthways. When gas cannot be procured, an oil lamp or wax candle may be used. An oil lamp proper for blowpipe operations can be obtained at any of the shops where they sell chemical apparatus—it need not, therefore, be described; it will be sufficient to say that it must have a broad and moderately thick wick, and that on each occasion the wick must be trimmed* before employing the flame for the blowpipe experiments. The best kind of oil for the lamp is pure rape or olive oil. The flame of a wax candle is far inferior in size and intensity to that of a lamp. Bunsen's lamp is described at par. 1167.

1151. Supports.—Various materials are used as supports for substances during the time they are exposed to the blowpipe flame; the principal are charcoal, platinum wire and foil, and glass tubes. The kind of support is regulated by the change we wish to effect upon the substance under examination.

1152. Charcoal.—The properties which make charcoal so valuable as a material for supports in blowpipe experiments are—1st, its infusibility; 2nd, its low conducting power for heat, which permits substances being heated more strongly upon a charcoal than upon any other kind of support; 3rd, its porosity, which makes it imbibe readily fusible substances, such as borax, carbonate of soda, &c., whilst infusible bodies remain on the surface; 4th, its power of reducing oxides, which greatly contributes to effecting the reduction of oxides in the inner blowpipe flame.

---

* The wick must be evenly cut and perfectly free from all extraneous fibres.

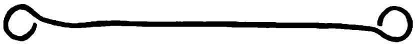
1153. Charcoal supports are used principally in the reduction of metallic oxides, &c., or in trying the fusibility of bodies. The substance to be subjected to the blowpipe flame —which, if in powder, should be previously moistened with a little water to make it cohere—is placed in a shallow hole made in the charcoal either with a knife or with a proper charcoal borer, and the charcoal is so held that the flame may impinge upon it at an angle of about 20 degrees. Metals that are volatile at the heat of the reducing flame evaporate wholly or in part upon the reduction of their oxides; in passing through the outer flame the metallic fumes are reoxidized, and the oxide formed is deposited around the portion of the matter upon the support. Such deposits are called incrustations. Many of these exhibit characteristic colours leading to the detection of the metals.

1154. Charcoal made from light woods—as the alder and pine—is the best for blowpipe experiments. It must be well-burned; it must be compact and free from crevices; it must not scintillate, smoke, or burn with flame; and it must of course, be perfectly dry. It should be cut by a small-toothed saw into pieces about six inches in length and from one to two inches in breadth, having a flat smooth surface at right angles to the rings of growth. It is this surface which is always to be used; and a good piece of charcoal may be made to serve for repeated experiments by simply filing off the used surface, and exposing a new one after each operation. As it is very difficult to get charcoal sufficiently good for blowpipe experiments, Mr. John J. Griffin has provided an excellent substitute, an account of which is given in pars. 1160 to 1167.

1155. *Platinum.* Platinum wire, and occasionally platinum foil, is used in all oxidizing processes before the blowpipe, and also when fusing substances with fluxes, with a view to try their solubility in them and to watch the phenomena attending the solution and mark the colour of the bead; lastly, also to introduce substances into the flame, to see whether they will colour it.

1156. The ends of the wire are twisted into a small loop (fig. 5), and when required for use, the loop is moistened with a drop of water, then dipped into the powdered flux (when a flux is used), the portion adhering to the wire is then exposed to the flame of a gas or spirit-lamp, when fused, and whilst still hot, it is dipped again into the powdered flux, and this is continued until the loop is completely filled with the flux after it has been fused. The bead when cold is moistened again, and a small portion of the substance to be examined put on and made to adhere to it by the action of a gentle heat. The loop is then finally exposed, according to circumstances, to the inner or to the outer blowpipe flame.

Fig. 5.



1157. A great many metallic oxides dissolve in borax, forming coloured glasses. If any metallic arsenides or sulphides are present in the substance which has to be examined with borax, the substance must be roasted by the method described in the next par. before making the examination with borax; and it is frequently advantageous, before roasting the powdered substance, to mix it with a little powdered charcoal, so as to prevent the formation of sulphates and arseniates.

1158. *Glass tubes.* Tubes of hard German glass of about a quarter of an inch internal diameter, five or six inches long, and open at both ends, are used in blowpipe experiments principally for roasting substances containing sulphur, arsenic, selenium, antimony, tellurium, &c., which, when heated with access of air, evolve fumes which may be recognised by colour, odour and chemical reaction.

1159. *Small Glass Bulbs*, or what answers equally well, glass tubes closed at one end of about two and a half to three inches long, and from one eighth to one fourth of an inch internal diameter, are employed to test substances for water, mercury, sulphur, or other bodies which are volatilized by the application of heat without the access of air. The volatile products collect in the neck of the bulb or tube, and may be judged of by their colour, odour, &c.

1160. *Griffin's substitute for charcoal.* "The blowpipe experiments that require the assistance of charcoal may be divided into two classes. In the first class may be named the formation of beads with microcosmic salt, the trial of fusibility *per se*, and the roasting of the metallic compounds that contain such volatile elements as sulphur and arsenic. The second class of experiments is restricted to the fusion of minerals or metallic compounds with carbonate of soda, or with soda and borax, for the purpose of effecting particular combinations, or of procuring their metals in a state of regulus. For these two classes of experiments I make use of two different composition supports, the first of which I call *Supports for Fusions*, and the second, *Supports for Reductions.* They are alike in appearance. Each consists of two parts—an upper or combustible portion, and a base or incombustible portion. The former is the proper substitute for the ordinary charcoal, the under portion acting only as a crucible, in which the combustible portion is contained. I shall first describe the composition and formation of the supports, and afterwards show the way to use them.

1161. "The incombustible portion of both supports is made of fine pipeclay and charcoal powder, mixed in equal parts by weight with as much water, slightly thickened with rice paste, as is sufficient to form a stiff plastic mass.

1162. "The combustible portion of the *Support for Fusions* consists of—

"Charcoal, in fine powder .	12	parts.
Rice flour	$\frac{1}{2}$	"
Water, about . . .	8	"

The rice is boiled in the water to form a paste, with which the charcoal is afterwards mixed into a mass of the consistence of dough.

1163. "The upper part of the *Support for Reductions* consists of the following mixture:

"Charcoal, in fine powder .	9	parts.
Carbonate of soda, crystallized	2	"
Borax, crystallized . .	1	"
Rice flour	½	"
Water, about . . .	8	"

The water is boiled, the soda and borax are dissolved in it, and the rice is then added to form a paste, with which the charcoal is finally incorporated, and the whole well kneaded into a stiff mass. The mould in which these compositions are pressed to form the supports is made of boxwood.*

1164. "The principal points which require attention to ensure success in this process are to have the materials in the state of a very fine powder, and the moist compositions of a proper degree of consistency. If they are too soft, the support will not quit the mould without losing its form; if too dry, the particles of the support will not cohere. The proper state is found after a few trials. It is most convenient to begin by making the mixture too soft, and then drying it slowly till it is found to be hard enough to work easily. The composition is rolled into balls with the fingers. The moulds should be kept clean, and the forming parts of the pestle for the charcoal composition, and the ring, should be oiled. The point of the pestle for the clay composition must not be oiled, because grease prevents the adhesion of the combustible portion of the clay base. A pestle made on purpose for the operation, is used to remove the finished support from the mould, by pressure on the clay foundation.

1165. "When the support is taken from the mould, it is placed on a hot plate or sand-bath to dry, after which the rough edges are taken off by a rasp. It is then ready for use. The bottoms of *supports for reductions* are painted with red ochre mixed with rice paste, to distinguish these from the other kind.

---

* These moulds, and every other part of the apparatus, are sold by Mr. Griffin, and, I have no doubt, can be procured through any of the other dealers in chemical apparatus.

The size I have fixed upon is as follows:—height, half an inch; diameter at top, half an inch; at bottom, two fifths of an inch. The weight is about 16 grains, consisting of 10 grains of clay crucible, and 6 grains of combustible matter. I have tried several other sizes, but this I find to be the most generally convenient. Nevertheless, a higher temperature can be produced upon a smaller support; and I find that large masses of charcoal are not essential, since many blowpipe experiments can be finished during the combustion of only two grains of charcoal. When in use, they are supported by a handle made of wire, turned into the form of a ring; a piece of tobacco pipe can be used for the handle of the wire support.

1166. " The following is the method of using these supports.

"Firstly, the surface of one of the supports for fusion is heated before the blowpipe flame. The support continues to burn like an ordinary pastile, till it is consumed down to the clay: in this respect the support has a superiority over common charcoal, which soon ceases to burn when removed from the fire. The ignited support is then to be rested upon a porcelain capsule, and a quantity of microcosmic salt, sufficient to form a bead, is placed on its red-hot surface. The salt instantly melts, and sinks into the central cavity, so as to form a bead; the heat, the form, and the smoothness of the surface of the support, facilitating this part of the process. The salt is then heated before the blowpipe, till it is converted into a transparent, colourless bead. The support is again placed on the porcelain capsule, and the metallic substance intended to be incorporated with the bead is added to it. The support continuing to be red-hot, and the bead consequently continuing soft, the substance so added is immediately absorbed, and its loss by dispersion prevented; whereas, upon common charcoal the fused salt solidifies soon after it is removed from the flame: and the substance added for examination, not adhering to it, is often blown away by the first blast from the blowpipe jet. The bead is now again fused, till the substance added to it is decomposed, and the resulting glass is observed to fuse quietly. It is then ready for examination; but it is sunk in the bottom of the hollow of the support, and cannot be seen by transmitted light, unless the projecting sides of the support be removed. This is effected as follows: the support is placed, as before, on the porcelain capsule, and the operator blows with his mouth, without the blowpipe, strongly down upon his surface. The pastile then burns away rapidly, and the force of the blast disperses the ashes, until the whole rim of the support is consumed. The bead then appears situated on the summit of a cone, and can be examined either by reflected or transmitted light. It is also in a position adapted for exposure to the different action of the oxidating and reducing flames, so as to have the character of the included metal fully developed. If, finally, the charcoal is allowed to burn wholly away, the coloured bead can be lifted from the ashes and preserved in a glass tube for subsequent examination and comparison.

"Secondly, if the surface of one of the *supports for reductions* be heated before the blowpipe, it becomes at first like the simple charcoal support; but in proportion as the charcoal is consumed, the fluxes which were mixed with it, and which are not volatile, concentrate and fuse upon the surface of the residue. If, therefore, a reducible metallic compound is heated upon such a support, it becomes at once exposed to the reducing action of the high temperature, of the nascent oxide of carbon, and of the carbonate of soda, whilst any earthy matter that it may contain is vitrified by the attendant borax."—*Griffin*.

1167. *Bunsen's gas-lamp.*—This gas-lamp with non-luminous flame is represented in fig. 1 of the Plate, and must be made exactly to scale, 3½ times as large as the drawing. It must be furnished with a cap at *a* for closing and opening the draught-holes, so as to be able to regulate the supply of air for every dimension of the flame. The conical chimney, *d d d d*, fig. 2, must also be made of such a size that the flame burns perfectly steady. Fig. 2 of the plate represents this flame of its natural size. It is composed of the following three chief divisions:

A. The *dark cone*, *a a a*, containing the cold unburnt gas mixed with about 62 per cent.

B. The *flame-mantle*, *a c a b*, formed of the burning coal-gas mixed with air.

C. *The luminous point*, *a b a*, not seen when the lamp is burning with the draught-holes open, but obtained of the size required for the reactions by closing these holes up to a certain point.

The following six points in the flame are used in the reactions:

1. *The base of the flame* lies at α; its temperature is comparatively very low, as here the burning gas is cooled by the upward current of cold air, and much heat is absorbed by the cold end of the metal tube. If mixtures of flame-colouring substances are held in this part of the flame, it is often possible to vaporize the most volatile constituent, and thus in the first few moments to obtain tints which cannot be observed at higher temperatures, because they then become masked by colours produced by the volatilization of the remaining substances.

2. *The zone of fusion* lies at β, somewhat above the first third of the flame in height, and midway between the inner and outer limits of the mantle at the point where the flame is thickest. This is the point in the flame which possesses the highest temperature, and it is therefore used in testing substances as regards their melting-point, their volatility, emissive power, as well as for all processes of fusion at high temperatures.

3. *The lower oxidizing flame* lies at γ, in the outer margin of the zone of fusion, and is especially suitable for the oxidation of substances dissolved in beads of fused salts.

4. *The upper oxidizing flame* at δ is formed by the highest point of the non-luminous flame, and acts most powerfully when the draught-holes of the lamp are wide open. This flame is suited for the oxidation of larger portions of substance, for roasting off volatile oxidation-products, and generally for all

those cases of oxidation in which an excessively high temperature is not needed.

5. *The lower reducing flame* lies at δ, on the interior edge of the mantle next to the dark central zone. As the reducing gases at this point are mixed with unburnt atmospheric oxygen, many substances remain here unaltered which become deoxidized on exposure to the upper reducing flame. This point of the flame gives, therefore, very valuable reactions which cannot be obtained with the blowpipe. It is especially available for reductions on charcoal, and in beads of fused salts.

6. *The upper reducing flame* is formed by the luminous point η, produced over the dark zone when the admission of air is lessened by the gradual closing of the draught-holes (fig. 1, *a*). If this luminous point is made too large, it will be found that a test-tube filled with cold water becomes covered with a film of lamp-black: this never ought to occur. This flame contains no free oxygen, is rich in finely divided incandescent carbon, and hence it possesses far more powerful reducing-powers than the lower reducing flame. It is especially available for reducing metals when it is desired to collect them in the form of films.

METHOD OF EXAMINATION IN THE VARIOUS PARTS OF THE FLAME.

A. *Behaviour of the Elements at High Temperatures.*[*]

1168. This is one of the most important reactions which can be employed for the detection and separation of substances. The possibility of producing, with the flame of the lamp alone, a temperature as high as or higher than that of the blowpipe depends upon the fact that the radiating surface of the heated body be made as small as possible. The arrangement for bringing the substances into the flame must therefore be on a very small scale. The platinum wire upon which the substance is heated must scarcely exceed the thickness of a horsehair, and one decimetre in length of the wire must not weigh more than 0·034 grm. It is impossible to obtain the results hereafter detailed if a thicker wire than this is employed. Substances which act upon platinum, or which will not adhere to the moistened surface of the metal, are held in the flame upon a thin thread of asbestos, of which a hundred may be obtained from one splinter of the mineral. These threads must not exceed in thickness one-fourth of that of an ordinary lucifer-match. Decrepitating substances are ground to the finest powder on the porcelain lamp-plate with the elastic blade (*a*) of the knife (fig. 4), and drawn up on to a moistened strip of one square centimetre of filter-paper. If the paper is then burnt, being held with the platinum forceps, or, better, between two rings of fine platinum wire, the sample remains as a coherent crust, which now may without difficulty be heated in the flame.

---

[*] For further information with regard to the flame reactions the student is referred to the translation of Bunsen's paper by Professor Roscoe in the 'Philosophical Magazine,' for 1867.

1169. If the substance requires to be heated in the flame for a long period, the holder (fig. 5) is used. The arm (*a*) is fastened to the carrier (A), so fixed on the stand by a spring (as seen at B) that it can be moved both horizontally and vertically. The glass tube (fig. 6) is held on this arm (*a*), and the fine platinum wire fused on to the tube thus held in the flame. The splinters of asbestos are stuck into the glass tube (*b*), which slips into the holder, and may then be moved with the carrier (A). The carrier (B) carries a spring-clamp for holding test-tubes which have to be heated for a considerable time in a particular part of the flame. The little turntable (C) contains nine upright supports to hold the wire tubes (fig. 6) employed in the experiments. By means of these arrangements a particle of the substance under examination is brought into the flame, and its behaviour in the coldest and hottest parts of the flame is ascertained, the substance being examined with a lens after each change of temperature. The following six different temperatures can be obtained in the flame, and these points may be judged of by observing the tints attained by the thin platinum wire:—

1. Below a red heat.
2. Commencing red heat.
3. Red heat.
4. Commencing white heat.
5. White heat.
6. Strong white heat.

It is scarcely necessary to remark that these different temperatures must not be ascertained by the glow of the substances themselves, as the luminosity of different bodies depends not only upon the temperature, but also mainly upon their specific power of emission.

1170. The following phenomena are observed when a sample of a substance is heated:—

1. *Emission of Light.*—The emissive power of substances is ascertained by placing them on the platinum wire in the hottest part of the flame. The sample is of weak emissive power when it is less luminous than the platinum wire, of a mean emissive power when both appear about equally luminous, and of strong emissive power when the intensity of the light which it emits is greater than that from the platinum. Most solid bodies emit a white light, others (as, for instance, erbia) coloured light.

Some bodies, such as many osmium, carbon, and molybdenum compounds, volatilize and separate out finely divided solid matter, which renders the flame luminous. Gases and vapours always exhibit a smaller power of emission than fused substances, and these generally less than solid bodies. The form of the substance under examination must always be noted, as the emissive power depends upon the nature of the surface: thus compact alumina, obtained by slowly heating the hydrate, possesses only a moderate emissive power, whereas the porous oxide prepared by quick ignition of the sulphate possesses a high power of emission.

2. *The melting-point* is determined by using the six different

temperatures already mentioned. At every increase of temperature the bead is examined with the lens to see whether the volume is decreased or increased, whether bubbles are given off on melting, whether, on cooling, the bead is transparent, and what changes of colour it undergoes during the action of the heat or on afterwards cooling.

3. *The volatility* is ascertained by allowing equally heavy beads of the substance, placed on a platinum wire, to evaporate in the zone of fusion, and observing the time, by means of a metronome, which the bead takes to volatilize. The point at which the whole of the substance is converted into vapour can be ascertained with great accuracy, often to a fraction of a second, by the sudden disappearance of the coloration of the flame. The platinum wire upon which the substance is weighed is protected from the moisture of the air by insertion in a tube (fig. 7). If we know the weight of the tube and wire, the right weight of substance can easily be attached, either by volatilizing a portion or by fusing some more substance on to the bead, and thus making it lighter or heavier. The experiments are best made with one centigramme of substance. The position in the flame where the highest constant temperature exists can be found by moving a fine platinum wire, fixed on a stand and bent at its point at a right angle, slowly about the zone of fusion, and noting the point where it glows most intensely. The beads to be volatilized are then most carefully brought into the flame at the same distance from the point of this wire. Care must also be taken that the dimensions of the flame do not undergo change from alterations in the pressure of the gas whilst the experiments are going on.

4. *Flame-coloration.*—Many substances which volatilize in the flame may be detected by the peculiar kinds of light which their glowing gases emit. These colorations appear in the upper oxidizing flame when the substance causing them is placed in the upper reducing flame. Mixtures of various flame-colouring substances are tested in the lowest and coldest part of the flame; and here it is often possible to obtain for a

few moments the peculiar luminosity of the most volatile of the substances unaccompanied by that of the less volatile constituents.

B. *Oxidation and Reduction of Substances.*

1171. In order to recognise substances by the phenomena exhibited in their oxidation and reduction, and to obtain them in a fit state for further examination, the following methods are employed:—

1. *Reduction in glass tubes* is especially employed for the detection of Hg, or for the separation of S, Se, P, &c., when in combination with Na or Mg. A stock of very thin glass tubes is prepared, each 2 to 4 millims. in width and 3 centims. in length: forty of these are easily made out of one ordinary-sized test-tube, by softening the glass before the blowpipe, and then drawing it out until the requisite size of tube is obtained. This long tube is then cut up with a diamond into pieces 6 to 8 centims. long, and each of these again divided into two over the lamp, and the closed ends neatly rounded. The sample having been finely powdered with the knife-blade (fig. 4, *a*) on the porcelain plate (fig. 3), is treated in a tube either by itself, or with a mixture of carbon and soda, or with Na or Mg. A piece of magnesium wire, a few millims. in length, is for this purpose pushed down into the powdered sample contained in the glass tube; the sodium is carefully freed from rock oil, and rolled out between the fingers to a small cylinder, which is then surrounded by the powdered substance. The best form of carbon is the soot from turpentine, which has been deposited upon the outside of a basin filled with cold water. As soon as the small tube containing the perfectly dry sample has been heated to the point of fusion of the glass, when generally an ignition inside the tube is noticed, it is allowed to cool and then placed upon the porcelain plate, covered by a piece of paper and crushed to powder with the knife, for the purpose of further examining the products of reduction.

2. *Reduction on splinters of Charcoal.*—In this way the

metal can be obtained in small globules, or as a porous mass, from quantities often less than a milligramme of the sample.

A transparent crystal of sodic carbonate is brought near to the outside of the flame, and a common wooden lucifer-match then rubbed over two-thirds of its length with the drops of fused salt. If the match is then turned upon its axis through the flame, the carbonized wood becomes surrounded with a crust of solid sodic carbonate, which, on heating in the zone of fusion, melts, and is absorbed by the carbon. A splinter of charcoal is thus obtained, which is prevented from burning by its glaze of soda. A mixture of the substance is then made with the knife upon the hand with one drop of the melted soda-crystal, and a portion of this, of the size of a mustard-seed, placed upon the point of the splinter. As soon as this has been melted in the lower oxidizing flame, it is passed through a part of the dark interior zone to the hotter portion of the lower reducing flame. The point at which the reduction occurs is easily seen by the violent effervescence of the soda; and this is after a time stopped by bringing the splinter into the dark zone. In order to isolate the reduced metal, the end of the splinter is broken off and rubbed up with a few drops of water in a small agate mortar, when the metallic particles are generally visible without removal of the carbon. For further examination, the carbon and soda can be easily removed by several careful washings, and the particles transferred to a small piece of curved glass cut out from an old flask,* in which they are again washed by decantation, the last drops of water removed by suction with a piece of filter-paper, and the metallic particles dried at a moderate heat. A few tenths of a milligramme of the metal is generally sufficient to yield a solution with which all the characteristic precipitations can be accomplished, the reagents being contained in capillary glass threads, dropped into the solution by the milligramme, and the effect thus produced ascertained by examination with a lens. Iron, cobalt, and nickel, which do not fuse to globules on the splinter, are withdrawn from the agate mortar by means of the point of the magnetized blade (fig. 4, *b*), washed with water, and dried high above the flame on the point of the knife. If the blade be then tightly drawn between the upper part of the thumb and the lower part of the first finger, and if the point of the blade be then approached to the metallic particles on the finger, they jump from the hand to the blade, forming a brush-like bundle, which can be conveniently examined by the lens, and by touching with a melted borax-bead can be transferred in suitable quantities. The portion of metal remaining on the knife is rubbed on to a small piece of filter-paper, a drop of acid added, and the paper warmed over the flame so as to allow the metal to dissolve; this solution can then be further examined with various reagents.

---

* Watch-glasses crack much too readily to be used for such experiments.

3. *Films upon Porcelain.*—Those volatile elements which are reduced by carbon and hydrogen can be deposited from their compounds as films on porcelain either in the elementary state or as oxides. Such films can be extremely easily converted into iodides, sulphides, and other compounds, and thus may be made to serve as most valuable and characteristic tests. The films are composed in the centre of a thick layer, which on all sides gradually becomes thinner until the merest tinge is reached; it is therefore necessary to distinguish between "thick" and "thin" parts of the films. Both exhibit in their variation of thickness all the tints of colour characteristic of the substance under different circumstances of division. One tenth up to one milligramme is in many cases sufficient for these reactions. Many surpass Marsh's arsenic test in delicacy and certainty, and approach in this respect the spectrum-analytical methods.

The following films can be obtained:—

(*a*) *Metallic films* are prepared by holding in one hand a particle of the substance on an asbestos-thread in the upper reducing flame, which must not be too large, whilst with the other hand a glazed porcelain basin, 1 to 2 decimetres in diameter, filled with cold water, is held close above the asbestos-thread in the upper reducing flame. The metals separate out as dead-black or brilliantly-black films of varying thickness. Even Pb, Sn, Cd, and Zn yield in this way films of reduced metal, which by mere inspection cannot be distinguished from the soot separated out on the porcelain by a smoky flame. By means of a glass rod, these films can be touched with a drop of dilute HNO_3, containing about 20 per cent. of real acid; and the various degrees of solubility of the films serves as a distinguishing characteristic.

(*b*) *Oxide-films* are obtained by holding the porcelain basin filled with water in the *upper oxidizing flame*, the rest of the operation being the same as in the production of the metallic films. If only a very small quantity of the sample can be employed, care must be taken to lessen the size of the flame, in order that the volatile products may not be spread over too large a surface of porcelain.

The film of oxide is examined as follows:—

(*α*) The colour of the thick and thin film is carefully observed.

(*β*) The reducing action or otherwise of a drop of stannous chloride is noted.

(*γ*) If no reduction occurs, NaHO is added to the stannous chloride until the precipitated hydrate redissolves, and then it is to be observed whether a reduction occurs.

(*δ*) A drop of perfectly neutral silver-nitrate is rubbed over the film with a glass rod, and a current of ammoniacal air is blown over the surface from a small wash-bottle containing ammonia solution, and having the mouth-tube dipping under the liquid and the exit-tube cut off close below the cork. If a precipitate is formed, the colour is observed, and the solubility or alteration, if any, noticed which occurs when the current of alkaline air is continued, or when a drop of ammonia-liquor is added.

(*b*) *Iodide-films* are simply obtained from the oxide-films by breathing on the latter upon the cold basin, which is then placed upon the wide-mouthed well-stoppered glass (fig. 8) containing fuming hydriodic acid and phosphorous acid derived from the gradual deliquescence of phosphoric triiodide.

When the mixture no longer fumes, owing to absorption of moisture, it is easy to render it again fuming by adding a little phosphoric anhydride. Other films, often containing both iodides of a metal, and therefore frequently less regular in colour and appearance, may be easily obtained by smoking the oxide-film with a flame of alcohol containing iodine in solution placed upon a bundle of asbestos-threads and held under the basin. If any iodine be condensed on the basin with the HI. it can easily be removed by gentle warming and blowing.

The examination of the film is conducted as follows:—

(α) The solubility of the film is examined simply by breathing upon it when the basin is cooled; the colour then either changes or entirely disappears, the film being dissolved in the moisture of the breath. If the basin be gently warmed, or if it be blown upon for some distance, the film again becomes visible by the evaporation of the moisture in the current of air.

(β) The ammonia compound of the iodide is formed by blowing ammoniacal air upon it, and noticing whether the colour of the thick and thin films alters quickly, slowly, or not at all. The different colours reappear at once if the basin be held for a few moments over an open bottle containing fuming HCl.

(γ) The iodide-films generally give the same reactions as the oxide-films with silver-nitrate and ammonia, with stannous chloride, and with caustic soda.

(*b*) The *sulphide-film* is most easily obtained from the iodide-film by blowing upon it a current of air saturated with ammonic sulphide, and removing the excess of sulphide by gently warming the porcelain. It is advisable to breathe on the film from time to time whilst the current of sulphuretted air is being blown on the basin. The experiments to be made with this film are:—

(α) The solubility or otherwise in water is ascertained by breathing on to it, or by addition of a drop of water. The sulphides often possess the same colour as the iodide-films; they may, however, generally be distinguished by their insolubility on breathing.

(β) The solubility of the sulphide in ammonic sulphide is ascertained by blowing or dropping.

(*b*) *Films on Test-tubes.*—Under certain circumstances it is advisable not to collect the film on porcelain, but upon the outside of a large test-tube (fig. 5, *e*); this method is especially used when it is needed to collect larger quantities of the reduction film for the purposes of further examination. The fine asbestos-thread with the sample of substance is held on the glass tube (*b*) before the lamp so that it is placed at the height of the middle of the upper reducing flame, and the test-tube fixed so that the lowest point is just above the end of the asbestos-thread. If the lamp be now pushed under the test-tube, the substance and the asbestos-thread are in the reducing flame. By repeating this operation the film can be obtained of any wished-for thickness; some pieces of marble are in this case placed in the test-tube, to prevent the water from being thrown out of the tube by percussive boiling.

III. The Reactions of the Elements.

1172. The elements, which can easily be recognised by their flame reactions, are arranged in the following groups and subgroups according to their behaviour in the reducing and oxidizing flames:—

A. Elements which are reducible to metal and are deposited in films.

1. Films scarcely soluble in cold dilute nitric acid—tellurium, selenium, antimony, arsenic.
2. Films slowly and difficultly soluble in cold dilute nitric acid—bismuth, mercury, thallium.
3. Films instantly soluble in cold dilute nitric acid—cadmium, zinc, indium.

B. Elements reducible to the metallic state, giving no film.

1. Not fusible to a metallic bead.
    - *a.* Magnetic—iron, nickel, cobalt.
    - *b.* Non-magnetic—palladium, platinum, rhodium, iridium.
2. Fusible to metallic beads—copper, tin, silver, gold.

C. Elements most easily separated and recognised as compounds—tungsten, titanium, tantalum and niobium, silicon, chromium, vanadium, manganese, uranium, sulphur, phosphorus.

APPARATUS REQUIRED IN PHOTO-CHEMICAL EXPERIMENTS.

1173. A large number of substances are volatilized when a small particle of the substance in the solid state is introduced into the inner flame of a gas or spirit-lamp. Many of these substances in volatilizing colour the outer flame, and as the colour imparted to the flame is in most cases different and distinct for each substance, the coloration of the flame has long been employed in chemical analysis as a test for many substances. Thus—Soda and its salts impart to the flame a yellow, potash and its salts a violet, strontia and its salts a crimson colour. The intensity of the colour of the salts of the same base, varies with their volatility, the most volatile of the salts producing the most intense coloration. Difficultly volatile salts produce only a slight, and non-volatile salts no coloration; thus, with silicates and other non-volatile compounds, such as are met with in nature, it is often difficult to detect 3 or 4 per cent. of the alkalies. In such cases the coloration may frequently be produced by adding some other substance which has the power of decomposing the compound under examination, and forming, with the substance we wish to detect, a compound which will volatilize at the temperature of the flame. If we add, for instance, to silicates containing only 3 or 4 per cent. of the alkalies, a little *pure* gypsum, this will decompose the silicate, a volatile alkaline sulphate, which will impart a colour to the flame, being formed.

1174. As the colour produced by one substance interferes or entirely obscures that produced by another, we were formerly unable to detect more than one body in a mixture of substances by means of the colour imparted to the flame. This defect has lately been overcome by looking at the coloured flame through coloured media, as coloured glasses and coloured liquids, which intercept the colour produced by one substance, whilst they allow the colour produced by another substance to pass. Thus, the yellow colour produced by sodium compounds obscures the violet produced by potassium ones; Cartmell, who was the first to employ coloured media, proposed, in order to detect potash in the presence of soda by means of the coloured flame, to view the flame through a blue glass stained with cobalt: through this coloured glass no coloured rays from soda (or lithia) can pass, but it admits those peculiar to potash.

1175. A solution of indigo can also be employed for the same purpose, Cartmell, for instance, detected lithia in the presence of soda and potash, by comparing the mixed colour of the flames of those bases with that of the flame of pure potash, when both are viewed through an indigo solution. Bunsen has found that the discrimination of these bases in presence of each other is more easily effected by observing the *succession of changes of colour*, which the mixed flame produced by these substances experiences when the rays reach the eye after passing through gradually thicker layers of an indigo solution. For this purpose a hollow plate glass prism (fig. 6) is used, filled with indigo solution; it is 40 millimetres high, and its principal section is a triangle, with two sides of a 150 millimetres, and the other of 35 millimetres. The indigo solution is made by dissolving 1 part of indigo in 8 parts of fuming sulphuric acid, diluting with 1500 to 2000 parts of water, and filtering.

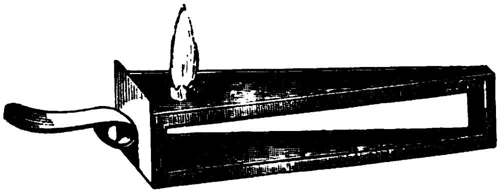


Fig. 6.

1176. In the following experiments the prism was moved horizontally before the eye, so that the rays of the flame always passed through gradually thicker layers of the medium. The alkaline substances, brought singly into the melting-space, exhibited the following changes:

1. *Chemically pure* $CaCl_2$ produces a yellow flame, which, even with very thin layers of the indigo solution, passed through a tinge of violet into the original blue lamp flame.

2. *Chemically pure* NaCl, the same.

3. *Chemically pure* K_2CO_3 *or* KCl appears of a sky blue, then violet, and at last of an intense crimson red, even when seen through the thickest layers of solution. Admixtures of soda or lime do not hinder the reaction.

4. *Chemically pure* L_2CO_3 *or* LCl gives a carmine-red flame, which, with increasing thickness of the medium, becomes gradually feebler, and disappears before the thickest layers pass before the eye. Lime and soda are also without influence on this reaction.

1177. Merz has proposed employing, in addition to the cobalt blue glass, a *violet*, a *red*, and a *green* glass; the violet glass is tinted with manganesic oxide; the red glass (partly coloured and partly uncoloured) with cuprous oxide, and the green glass with ferric and cupric oxides. The common coloured window glass will generally be found to answer the purpose of the green glass.

REAGENTS.

1178.—LIST OF THE REAGENTS EMPLOYED IN THE FLUID STATE.

1. HCl, *Hydrochloric acid* (muriatic acid), if *pure*, is perfectly colourless, and leaves no residue when evaporated; its sp. gr. should be 1·2. The substances with which it is generally contaminated are Fe, As, and H_2SO_4. It may also contain Cl and SO_2.

If it gives, after dilution with distilled water, a precipitate with $BaCl_2$, H_2SO_4 is present. If it turns yellow on evaporation, or if, after adding NH_4HO in excess, then acidifying with acetic acid, it gives a blue colour after the addition of a solution of potassic ferrocyanide, it contains Fe'''. If it imparts a blue tint to a solution of KI mixed with starch paste, it contains Cl, and if it discolours a fluid made faintly blue with iodide of starch, it contains SO_2. Examine it for As by Marsh's test, described in the fifth group of bases.

Dilute one part of the concentrated acid with two parts of water.

2. HNO_3, *Nitric acid* (aqua fortis), when free from non-volatile matter, leaves no residue on evaporation; its sp. gr. should be 1·517. The impurities often found in it are HCl and H_2SO_4.

If, after dilution with distilled water, it gives a precipitate with $BaCl_2$, H_2SO_4 is present; and if the diluted acid gives a precipitate with $AgNO_3$, HCl is present.

Dilute one part of the concentrated acid with two of water.

3. *Nitro-hydrochloric acid* (aqua regia) is prepared by adding four parts of concentrated hydrochloric acid to one of concentrated nitric acid.

"Nitric acid and hydrochloric acid decompose each other, the decomposition, mostly resulting, as *Gay Lussac* has shown, in the formation of two compounds which are gaseous at the ordinary temperature, $NOCl_2$ (chloronitric acid), and NOCl (chloronitrous gas), and of Cl and water. If one equivalent of HNO_3 is used to three equivalents of HCl, it may be assumed that only chloronitric acid ($NOCl_2$), Cl and H_2O are formed ($HNO_3 + 3HCl = NOCl_2 + Cl + 2H_2O$). This decomposition ceases as soon as the fluid is saturated with the gas; but it recommences the instant this state of saturation is disturbed by the application of heat or by decomposition of the acid. The presence of the Cl, and also, but in a very subordinate degree, that of the acids named, makes aqua regia the most powerful solvent for the metals (with the exception of those which form insoluble chlorides."

This test is employed in an undiluted state.

4. H_2SO_4, *Sulphuric acid* (oil of vitriol), frequently contains As, Pb, Fe''', Ca, and oxides of nitrogen. The Pb is deposited to a great extent when the acid is diluted, $PbSO_4$ being less soluble in dilute than in concentrated H_2SO_4.

This acid ought to leave no residue upon evaporation on platinum; and if it does not remain perfectly clear upon dilution with four or five parts of spirits of wine, $PbSO_4$, $Fr_2'''3SO_4$, or $CaSO_4$ is present. "The presence of small quantities of Pb is detected most easily by adding some HCl to the H_2SO_4 in a test tube; if the point of contact is marked by turbidity ($PbCl_2$), Pb is present." If a solution of $FeSO_4$ is poured upon some of the acid in a test tube, so that the iron solution floats upon the acid, a purplish red ring will be formed at the junction of the two solutions, if the acid contains nitric or hyponitric acid. If, after dilution with 20 parts of water, it imparts a blue tint to a solution of KI, mixed with starch paste, hyponitric acid is present. Examine it for arsenic by Marsh's test, described in the fifth group of bases.

Fresenius recommends the following process for the preparation of pure sulphuric acid:—Take of strong sulphuric acid 1000 grm., ammonic sulphate 3 grm., manganic peroxide in powder 5 grm., put the acid in a porcelain dish, add the ammonic sulphate, and heat till copious fumes of H_2SO_4 escape; this is done to destroy any oxides of nitrogen. After cooling, add the manganic peroxide, and heat to boiling, with stirring, in order to convert any arsenious into arsenic acid. When cool, pour off the clear fluid into a retort about a litre in capacity, and distil. The neck of the retort must reach so far into the receiver that the distillate may drop directly into its body. The receiver should not be cooled with water. To prevent the neck of the retort from touching the receiver, some long asbestos may be used. When about 10 c. c. have been drawn over, change the receiver, and distil off three fourths of the contents of the retort. This method depends upon the fact that sulphuric acid containing arsenic in the form of arsenic acid, yields an arsenic-free distillate.

The dilute acid is prepared by adding four parts of water to every one of the concentrated acid.

5. $H_2C_4H_4O_6H_2\overline{T}$, *Tartaric acid* is generally sufficiently pure for analytical purposes. As it undergoes decomposition in solution, a small quantity only should be prepared at a time.

For use, dissolve one part, by weight, of acid, in two parts, by measure, of water.

6. $NaHC_4H_4O_6$, Sodic hydric tartrate is prepared by dissolving a quantity of tartaric acid in water, dividing the solution into two equal parts, and neutralizing one exactly with Na_2CO_3, and then adding the other portion, and afterwards evaporating the whole solution until the bitartrate crystallizes.

For use, make a saturated solution.

7. $HC_2H_3O_2=H\bar{A}$, *Acetic acid*, when employed in analysis, ought to leave no residue on evaporation, and after saturation with Na_2CO_3, emit no empyreumatic odour. It ought to give no precipitate with $BaCl_2$ and $AgNO_3$, and it ought to give no colour or turbidness with H_2S, or with $(NH_4)_2S$, after it has been neutralized with NH_4HO.

The ordinary commercial acetic acid is sufficiently concentrated for analytical purposes.

8. H_2S, *Hydrosulphuric acid* (sulphuretted hydrogen) is prepared by adding to FeS, in an appropriate apparatus, dilute H_2SO_4 or HCl. The H_2S is liberated in its gaseous state, and may be passed through any solution under examination; or a solution of the gas may be obtained by passing it through pure water. As this solution very soon decomposes by contact with the atmosphere, it ought to be prepared very frequently, and kept in well-stoppered bottles.

FeS, from which H_2S is obtained, is prepared by projecting a mixture of thirty parts of iron filings with twenty-one of flowers of sulphur, in small portions at a time, into a red-hot crucible, replacing the cover after each addition. When the whole has been added, the ignition must be continued for a short time, until the excess of sulphur has been dissipated. Bloxam has found that H_2S, prepared from FeS, contains arsenic, but if obtained from native sulphide of antimony and HCl it is free from it; it ought, in examination for poisons at least, always to be prepared from the antimony sulphide.

9. SO_2, *Sulphurous anhydride*, is prepared by acting upon copper or charcoal with sulphuric acid. For this purpose small pieces of charcoal are introduced into a flask, with from six to eight times their weight of H_2SO_4, and a moderate heat applied. The evolved gas must be conducted into cold water until it is no longer absorbed. On account of the great tendency which this reagent has to absorb more oxygen, and become converted into H_2SO_4, it must be preserved in well-stoppered bottles.

10. Cl, *Chlorine gas*, is prepared by mixing 18 parts of NaCl with 15 parts of finely powdered MnO_2; the mixture is placed in a flask and upon it is poured a *completely cooled* mixture of 45 parts of concentrated H_2SO_4, and 21 parts of water, the flask is then shaken. A uniform and continuous evolution of Cl will soon begin, which, when slackening, may be easily increased again by the application of a *gentle* heat. A solution of the gas may be prepared by passing it into cold water. Chlorine water must be kept in well stoppered bottles, and excluded from the light; for if exposed to light it is speedily converted into HCl, oxygen being evolved; when it has lost its odour it is unfit for use.

11. H_2SiF_6, *Hydrofluosilicic acid.* This acid is prepared as follows:—Take 1 part of sand, wash it and dry it thoroughly, mix it with 1 part of calcic fluoride, also dry and place the mixture in a flask; 6 parts of concentrated H_2SO_4, are then added. The mixture must only fill the flask one third as it swells up on being warmed; heat the flask by means of a sand-bath; a gas delivery tube dips into a vessel containing 4 parts of water and some mercury; the tube dips beneath the surface of the mercury, to prevent the tube from being stopped up by the silica which is formed when the silicic fluoride (SiF_4) comes in contact with water, the following diagrams express the chemical changes which ensue:—

(1) $SiO_2 + 2CaF_2 + 2H_2SO_4 = SiF_4 + 2CaSO_4 + 2H_2O$

(2) $3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$.

12. $H_2C_2O_4 = H_2\bar{O}$, *Oxalic acid.*—Dissolve one part, by weight, of the acid, in twenty parts, by measure, of water.

13. $(NH_4)_2C_2O_4$, *Ammonic oxalate,* ought to leave no residue after ignition on platinum foil, and it ought not to give a precipitate, nor be rendered turbid, by H_2S nor by $(NH_4)_2S$.

Dissolve one part, by weight, of the salt, in twenty-four parts, by measure, of water.

14. NH_4HO, *Ammonia,* must be colourless, and leave no residue upon evaporation to dryness. It ought not, after being diluted with three volumes of distilled water, to give a precipitate on the addition of lime water. It ought not, after being acidulated with pure HNO_3, to give a precipitate with $Ba(NO_3)_2$ nor with $AgNO_3$. H_2S ought not to impart to it the slightest colour, and on the addition to it of a few drops of a solution of ammonio-sulphate of copper, a black precipitate ought not to be formed.

15. NH_4Cl, *Ammonic chloride.*—This salt ought to volatilize completely when ignited on platinum foil; the solution ought to be neutral to test paper, and it ought to give no precipitate nor coloration on the addition of $(NH_4)_2S$.

Dissolve one part, by weight, of the salt, in eight parts, by measure, of water.

16. $(NH_4)_2S$, *Ammonic sulphide,* is prepared by passing hydrosulphuric acid through NH_4HO, until it does not produce a precipitate in a solution of $MgSO_4$. It ought not to produce a precipitate with a solution of lime, and it ought to leave no residue on evaporation to dryness and ignition.

17. *Ammonic carbonate* must completely volatilize. Its solution ought to give no precipitate or coloration with $(NH_4)_2S$ nor with H_2S after acidulation with HCl. Its solution, after being acidulated with HNO_3, ought to produce no precipitate with $Ba(NO_3)_2$ nor with $AgNO_3$.

Dissolve one part, by weight, of the salt, in four parts, by measure, of water, and add one measure of ammonia.

18. NH_4NO_3, *Ammonic nitrate,* is made by neutralizing HNO_3 with $(NH_4)_2CO_3$. The solution is evaporated until crystals begin to be deposited, and is then allowed to cool; the crystals are afterwards fused.

19. *Ammonic arseniate* is prepared by neutralizing arsenic acid with ammonic carbonate and evaporating to dryness.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

Arsenic acid is prepared by dissolving arsenious acid in HNO_3, mixed with a little HCl, evaporating the solution to dryness, and igniting somewhat below a *low* red heat until all HNO_3 is expelled.

20. *Ammonic molybdate in nitric acid.*—Dissolve one part of molybdic trioxide in eight parts of strong NH_4HO, or one part of acid ammonic molybdate in three parts of NH_4HO, with the aid of heat; pour the solution into twenty parts of HNO_3, consisting of equal parts of strong HNO_3 and water.

21. K_2SO_4, *Potassic sulphate.* — Recrystallize the K_2SO_4 of commerce; dissolve one part, by weight, of the purified salt in 200 parts, by measure, of water.

22. KNO_2, *Potassic nitrite*, may be prepared "by heating in a flask only half filled with the mixture two parts of starch, in pieces, with eight parts of impure HNO_3 of 1·4 sp. gr. and eight parts of water, and conduct the nitrous fumes* evolved first through a large empty flask, then into a flask containing a solution of KHO until it is completely saturated, If the potassic solution contains silicic acid or alumina, as is mostly the case, the saturation point is marked by the separation of these impurities. Five parts of solution of KHO of 1·27 sp. gr. is the quantity required in the process. As soon as the action begins, the flame under the evolution flask must be temporarily removed, or otherwise the action might become too energetic. Evaporate the filtered solution to dryness. Dissolve one part of the dry salt to about two parts of water when the reagent is required for use."

23. K_4FeCy_6, *Potassic ferrocyanide* (yellow prussiate of potash), is prepared on the manufacturing scale by adding animal matters, such as horns, feathers, dried blood, leather-clippings, &c., mixed with iron filings, to fused K_2CO_3, lixiviating the fused mass with water, then filtering and crystallizing

---

* Nitrous anhydride (N_2O_3) nearly in a state of purity.

by evaporation. The animal matter contains nitrogen and carbon, the latter in larger proportion than is required to form cyanogen with the nitrogen; hence when these substances are fused with K_2CO_3, the excess of carbon reduces the K_2CO_3; the K being set free, unites with the cyanogen formed from the N and the remainder of the C producing KCN, which is converted into the ferrocyanide by the action of the KCN on the Fe when the fused mass is heated with water.

The commercial K_4FeCy_6 is sufficiently pure for analytical purposes; dissolve one part by weight, in twelve, by measure of water.

24. $K_6Fe_2Cy_{12}$, *Potassic ferricyanide* (red prussiate of potash), is prepared by the action of oxidizing agents on the ferrocyanide. It is usually prepared by passing washed chlorine gas (with constant agitation to ensure uniformity of action) through a cold solution of the ferrocyanide until it no longer gives a blue but a brown colour with a ferric salt.

Dissolve one part, by weight, in twelve, by measure, of water; the solution ought to be made as it is wanted, as the ferricyanide decomposes when in a state of solution, a trace of ferrocyanide being formed.

25. NH_4CyS, *Ammonic sulphocyanide;* KCyS, *Potassic sulphocyanide.* — NH_4CyS may be prepared (1) by digesting HCy with ammonic polysulphide, prepared by digesting sulphur in $(NH_4)_2S$, taking care to keep the latter slightly in excess, which is indicated by the yellow colour of the solution, then boiling off the excess of the latter, filtering and evaporating to the crystallizing point:—$2CNH + (NH_4)_2S, S_2 = 2NH_4CyS + H_2S$. (2) A mixture of 750 parts of NH_4HO and 100 parts of CS_2 (carbonic disulphide), and 750 parts of alcohol, 86 per cent., is distilled down to one half after standing for 24 hours, the residual liquid is evaporated to the crystallizing point:—$4NH_4HO + CS_2 = NH_4CyS + (NH_4)_2S + 4H_2O$. Potassic sulphocyanide may be prepared by heating to low redness in a covered vessel a mixture of 46 parts of dried K_4FeCy_6, 37 parts of S, and 17 parts of pure K_2CO_3; the mass after heating is exhausted with water; the watery

solution is evaporated to dryness on the water-bath, and the residue is exhausted with alcohol, which deposits crystals on cooling or evaporation.

Dissolve 1 part, by weight, of either salt in 10 parts of water.

26. K_2CrO_4, *Potassic chromate*, in solution ought not, after it has been acidulated with HCl, to give a precipitate with $BaCl_2$.

Dissolve 1 part, by weight, in 8 parts, by measure, of water.

27. KCN = KCy, *Potassic cyanide*, is prepared by mixing intimately 8 parts of *anhydrous* potassic ferrocyanide and 3 parts of potassic carbonate, and introducing the mixture by small portions into a cast-iron crucible previously heated to low redness; after all the materials have been added, the crucible is kept in the fire till a sample of the fused mass taken out on a glass rod appears white, and exhibits the aspect of porcelain on cooling; the crucible is then removed from the fire and left at rest for a moment to allow the iron liberated by the decomposition to settle down; it is then poured out carefully, to prevent the running out of the minute particles of iron, into a clean iron or silver vessel. Thus prepared, it always contains a little potassic carbonate and cyanate. The potassic carbonate employed must be free from sulphate, as this would be reduced to sulphide by the cyanide. It may also be prepared by igniting the ferrocyanide *alone;* but as one third of the cyanogen in this case is resolved into carbon and nitrogen, only two thirds is obtained in the form of the salt.

28. NaHO, *Sodic hydrate* (caustic soda), is prepared by dissolving 1 part, by weight, of Na_2CO_3, in 9 parts, by measure, of water, and boiling the solution in a clean iron pan; milk of lime prepared by adding 1 part of CaO (quicklime) to 3 parts of boiling water, is then added in small portions to the boiling liquid, until HCl causes no effervescence in a portion of the clear liquid. When this point has been attained, the pan must be removed from the fire, and the precipitate allowed to subside. The supernatant liquid must then be drawn off by

means of a syphon, or passed through a filter of bleached linen, and the filtrate evaporated rapidly over a quick fire until it has been reduced to half its original bulk. On supersaturating a portion of the liquid with HCl, no, or only a slight, effervescence should take place. H_2S must not produce a precipitate or coloration in its solution. The solution must be evaporated until it has a sp. gr. of from 1·13 to 1·15; it must be kept in well-stoppered bottles.

29. Na_2CO_3, *Sodic carbonate*, in solution ought not, after it has been acidulated with HNO_3, to give a precipitate with $BaCl_2$ nor with $AgNO_3$.

Dissolve 1 part, by weight, of the salt, in 10 parts, by measure, of water.

30. Na_2HPO_4, *Disodic hydric phosphate*, must form no precipitate with ammonia.

Dissolve 1 part, by weight, of the salt, in 10 parts, by measure, of water.

31. $NaC_2H_3O_2$, *Sodic acetate*, is made by adding acetic acid to a concentrated solution of Na_2CO_3 until all effervescence ceases. This solution must be free from sulphates.

Dilute 1 part of the concentrated solution with 4 parts of water.

32. $NaHSO_3$, *Sodic hydric sulphite.*—Pass SO_2, prepared as directed at 9, page 400, through a bottle containing a small quantity of water, then into a flask containing a solution of Na_2CO_3 (prepared by dissolving 7 parts of the pure crystallized carbonate in from 20 to 30 parts of water) until CO_2 ceases to be evolved. The solution must be kept in a well-stoppered bottle, as it has a great tendency to absorb oxygen, and pass from sulphite to sulphate.

33. $Na_2B_4O_7(H_2O)_{10}$, *Borax*, is employed in blowpipe analysis. It should be heated below the fusing point to drive off its water of crystallization, and then powdered.

34. *Sodic* and *Potassic carbonate.*—Equal parts of these two carbonates in the anhydrous state must be mixed together. They must not contain any sulphate.

35. $NaNH_4HPO_4$, *Sodic ammonic hydric phosphate* (mi-

crocosmic salt).—This salt, which is found in human urine after putrefaction, and in guano from Ichaboe, may be prepared artificially in several ways; the following is a very convenient method:—6 or 7 parts of crystallized disodic hydric phosphate (Na_2HPO_4) and 1 part of NH_4Cl are dissolved in 2 parts of boiling water, the $NaNH_4HPO_4$ crystallizes out as the solution cools, the NaCl remaining in solution; the phosphate may be freed from NaCl by recrystallization from a small quantity of boiling water containing a little NH_4HO.

36. $K_2H_2Sb_2O_7$, *Dihydric dipotassic metantimoniate*, may be prepared by projecting a mixture of equal parts of powdered tartar emetic and potassic nitrate in small portions at a time into a red-hot crucible. After the mass is deflagrated keep it at a moderate heat for a quarter of an hour longer, then remove it from the fire, and when sufficiently cold treat it with warm water; transfer the mixture to a suitable vessel, and decant the *clear* fluid from the heavy powder and concentrate it. After one or two days a doughy mass will separate from the liquid; treat this mass with three times its volume of cold water, working it at the same time with a spatula. This operation will serve to convert it into a fine granular powder, to which add the powder from which the fluid was decanted, wash slightly, and dry on blotting-paper. Prepare the solution only immediately before it is required for use, by shaking the salt with cold water, and filtering off the fluid from the undissolved portion; it must be clear, and of neutral reaction; it must give no precipitate with solution of KCl, or with one of NH_4Cl, but must produce a crystalline precipitate with one of NaCl.

37. $BaCl_2$, *Baric chloride.*—A solution of this salt must be neutral to test-paper; after precipitation by H_2SO_4, the filtrate ought not to leave the slightest residue when evaporated on platinum foil. Its solution ought not to give a precipitate or be coloured by the addition of H_2S or by $(NH_4)_2S$.

Dissolve 1 part of the salt in 10 of water.

38. $Ba(NO_3)_2$, *Baric nitrate.*—A solution of this salt must

not be rendered turbid by $AgNO_3$; for other impurities, test as directed in $BaCl_2$.

Dissolve 1 part of the salt in 10 parts of water.

39. *Lime water* is made by digesting recently prepared CaH_2O_2 for some time with cold distilled water, with frequent agitation of the mixture; allow the undissolved portion of the lime to subside, decant subsequently, and keep the clear fluid in well-stoppered bottles.

40. $CaCl_2$, *Calcic chloride*, is made by dissolving pure $CaCO_3$ in dilute HCl; the solution thus obtained must be neutral to test-paper, and it must not form a precipitate, nor be coloured by $(NH_4)_2S$.

41. $CaSO_4$, $2H_2O$ *Calcic sulphate* (gypsum).—Dissolve as much of the salt as the water will take up.

42. $MgSO_4$, $7H_2O$, *Magnesic sulphate* (Epsom salts).—Dissolve 1 part in 8 of water.

43. $BaCO_3$, *Baric carbonate*, may be prepared by dissolving $BaCl_2$ in hot water, and precipitating by $(NH_4)_2CO_3$ and NH_4HO; the precipitate must be washed until the last washing gives no turbidness with $AgNO_3$. Stir the precipitate with water to the consistence of cream, and keep the mixture in a stoppered bottle; shake the mixture before using it.

44. $FeSO_4$, $7H_2O$, *Ferrous sulphate.*—The purified commercial salt is sufficiently pure; it is principally employed for the detection of nitric acid.

Dilute 1 part of the concentrated solution with 3 parts of water.

45. Fe_2Cl_6, *Ferric chloride*, is prepared by dissolving recently precipitated and well-washed $Fe_2H_6O_6$ in pure HCl; the ferric hydrate must be kept during the solution slightly in excess, as the ferric chloride must contain no free acid; it is afterwards diluted with an equal volume of water and filtered.

46. $Pb(C_2H_3O_2)_2$, *Plumbic acetate.*—The best commercial acetate is sufficiently pure to be used as a reagent; dissolve 1 part, by weight, of the salt, in 10 parts, by measure, of water.

47. $HgNO_3$, *Mercurous nitrate*, is made by gently heating in

a small flask 9 parts of HNO_3, in conjunction with 10 parts of Hg, until the disengagement of nitrous fumes ceases; the solution is then boiled for some time with the undissolved portion of the Hg, care being taken to replace the water lost by evaporation. The crystals, which separate on the cooling of the liquid, are dissolved in 20 parts of cold water, slightly acidulated with HNO_3. The fluid is then filtered if necessary, and the filtrate kept in a glass bottle, the bottom of which is covered with mercury.

48. $HgCl_2$, *Mercuric chloride.*—Dissolve 1 part of the salt in 16 parts of water.

49. $CuSO_4$, $5H_2O$, *Cupric sulphate.*—The commercial salt is purified by two or three crystallizations; dissolve 1 part, by weight, of the purified crystals, in 10 parts, by measure, of water.

50. *Ammonio-sulphate of copper* is prepared by adding NH_4HO, drop by drop, to a not too concentrated solution of $CuSO_4$, until the precipitate at first produced is nearly redissolved; the clear solution to be employed.

51. $AgNO_3$, *Argentic nitrate*, is prepared by dissolving pure Ag in pure HNO_3 diluted with an equal bulk of water, evaporating the solution to dryness and gently fusing the residue; if pure, its solution will, after addition of HCl in excess and filtering, leave no fixed residue. Dissolve 1 part, by weight, of the salt, in 20 parts, by measure, of water.*

52. *Ammonio-nitrate of silver* is prepared by adding NH_4HO, drop by drop, to a solution of $AgNO_3$, until the precipitate at first formed is nearly redissolved; the clear solution to be employed.

53. $Co(NO_3)_2$, *Cobaltic nitrate.*—This salt can be purchased fit for use; dissolve 1 part, by weight, in 10 parts, by measure, of water.

54. $PtCl_4$, *Platinic chloride.*—Purify platinum scraps by boiling them in HNO_3; when purified treat with concentrated HCl, and some HNO_3, in a narrow-necked flask and apply heat, add occasionally HNO_3 until the Pt is dissolved. Evaporate the

---

* See Appendix A, page 413.

solution on the water-bath, to dryness, adding during the evaporation HCl, dissolve the residue in 10 parts of water. Dry $PtCl_4$, if pure, dissolves completely in spirits of wine.*

55. $AuCl_3$, *Auric chloride.*—If the gold is perfectly pure it has simply to be dissolved in aqua regia, and evaporated to dryness over the water-bath, and the residue redissolved in water. If it contains silver, filter off from the insoluble AgCl, which will remain on treating the residue with water. If it contains copper, which may be ascertained by diluting a portion of the acid solution, and adding to it $K_4Fe_2Cy_{12}$, mix it with a solution of $FeSO_4$ in excess; collect the metallic gold, wash it, and then redissolve in aqua regia, and evaporate as before.†

56. $SnCl_2$, *Stannous chloride.*—Boil granulated tin in concentrated HCl in a flask, keeping the tin always in excess until H ceases to be evolved, then dilute the solution with four times its volume of water containing a little HCl, and filter. Keep the filtrate in a well-stoppered bottle containing some fragments of tin.

57. PbO_2, *Plumbic peroxide,* may be prepared by digesting in boiling HNO_3, diluted with four or five times its bulk of water, red lead in fine powder; the residue is washed with a fresh quantity of the dilute HNO_3, and then with water until everything soluble is removed.

58. *Copper turnings* are employed for the detection of nitric acid.

59. *Zinc* must be perfectly free from arsenic. Test for this impurity as directed at par. 262.

60. Nessler's test.—"This reagent is an aqueous solution of potassic iodide, saturated with mercuric iodide, and rendered powerfully alkaline with soda or potash. It is prepared by dissolving 50 grammes of KI in a small quantity of hot distilled water. The vessel containing this solution is placed on the water-bath, and to it is added a strong solution of $HgCl_2$, which will cause a red precipitate (HgI_2), that disappears on shaking the mixture. The $HgCl_2$ solution is carefully added,

---

* See Appendix B, page 414.

† See Appendix C, page 415.

the liquid being at the same time shaken, so as to dissolve the precipitate as fast as it is formed; the addition of the $HgCl_2$ solution is continued until the precipitate ceases to be dissolved. When this point is reached no more $HgCl_2$ must be added. The mixture is then filtered, and to the filtrate is added 150 grammes of solid NaHO in strong aqueous solution (or about 200 grammes of solid KHO dissolved in water). After the addition of the alkali solution, the liquid is diluted so as to make its volume equal to one litre. Add to the diluted liquid about 5 cub. cent. of a saturated aqueous solution of $HgCl_2$; allow to subside, and decant the clear liquid.

"As exposure to the air is apt to render this reagent somewhat turbid, it is advisable to keep the stock of the reagent in a large bottle, which should only be opened to supply a small bottle kept to hold that which is in immediate use. The addition of the 5 c. c. of solution $HgCl_2$ has two objects; it causes the reagent to clear rapidly, and imparts sensitiveness to the reagent when deficient in that quality." (Wanklyn and Chapman on 'Water Analysis.')

61. *Solution of indigo.*—"Take from 4 to 6 parts of fuming H_2SO_4, add slowly and in small portions at a time 1 part of finely pulverized indigo, taking care to keep the mixture well stirred. The acid has at first imparted to it a brownish tint by the matter which the indigo contains in admixture, but it subsequently turns blue. Elevation of temperature to any considerable extent must be avoided, as part of the indigo blue is thereby destroyed; it is therefore advisable, when dissolving larger quantities of the substance, to place the vessel in cold water. When the whole of the indigo has been added to the acid, cover the vessel, let it stand forty-eight hours, then pour its contents into twenty times the quantity of water, mix, filter, and keep the filtrate for use."

62. *Distilled water* ought always to be employed in all the above solutions and in all analytical operations. It should leave no residue on evaporation, and should give no precipitate, or even turbidity, with $BaCl_2$, $AgNO_3$, $(NH_4)_2C_2O_4$, or lime water.

63. *Reagent papers.*—Blue litmus paper serves to detect the presence of free acids or of acid salts in fluids, since they change the blue colour to red. Reddened litmus paper serves to detect the presence of free alkalies, and of earths and salts possessing an alkaline reaction, by changing the red colour to blue. Turmeric paper aids, like reddened litmus paper, in the detection of free alkalies, &c., by changing its yellow colour to brown.

Preparation of blue litmus paper.—"Digest 1 part of litmus of commerce with 6 parts of water, and filter the solution; divide the intensely blue filtrate into 2 equal parts; saturate the free alkali in the one part, by repeatedly stirring with a glass rod dipped in very dilute H_2SO_4, until the colour of the fluid just appears red; add now the other part of the blue filtrate, pour the whole fluid into a dish, and draw strips of fine, unsized paper through it; suspend these strips over threads, and leave them to dry. The colour of litmus paper must be perfectly uniform, and neither too light nor too dark."

Preparation of reddened litmus paper.—"Stir blue solution of litmus with a glass rod dipped in dilute H_2SO_4, and repeat this process until the fluid has just turned distinctly red. Steep slips of paper in the solution, and dry them as directed in the preceding paragraph. The dried slips must look distinctly red."

Vacher prepares a paper of neutral tint thus:—Digest 20 grm. litmus with 100 c. c. water for some days, shaking occasionally, then filter. To the filtrate add slight excess of HNO_3 and boil; then neutralize exactly with KHO. Now make a weak solution of gelatine by boiling 1 part of isinglass with 50 parts of water; draw white blotting-paper through this, and hang it up to dry. When dry, paint one side with the above solution.

Preparation of turmeric paper.—Digest and heat 1 part of bruised turmeric root with 6 parts of weak spirit of wine, filter the tincture obtained, and steep slips of fine paper in the filtrate. The dried slips must exhibit a fine yellow tint.

Schonbein's test-papers for hydrocyanic acid.—Three parts of resin of guaiacum are dissolved in 100 parts of rectified spirit; white filtering paper is steeped in this solution and dried. The paper should remain white. The solution of cupric sulphate, with which these papers are to be moistened just before being used, is prepared by dissolving one part of cupric sulphate in 500 parts of water.

Brazil-wood paper is prepared by moistening slips of fine writing paper with decoction of Brazil wood.

APPARATUS.

1179. The processes employed in qualitative analysis are exceedingly simple, and do not require much apparatus for their execution. The small amount actually requisite is described in the following list, and may be procured in the shops of operative chemists.

1½ dozen test tubes.
Test-tube stand.
2 small evaporating dishes.
Washing bottle.
Spirit lamp.
2 watch-glasses.
Rat-tail and triangular file.
Platinum wire and foil.
Sulphuretted hydrogen apparatus.
A number of best corks.
A few lengths of small vulcanized tubing.
Small retort stand.
3 small glass funnels.
2 porcelain crucibles.
½ lb. glass tubing.
¼ lb. glass rod.
Small mortar and pestle.
1 quire filtering paper.
Crucible tongs.
Black's blowpipe.
Tube cleaner.
Small german beakers.
Litmus paper, blue and red.
Turmeric paper.

APPENDICES.

Appendix A. Treatment of Silver Residues.—Waste solutions containing silver must not be poured into the sink, but into a bottle containing some commercial hydrochloric acid; when a quantity of the precipitated AgCl has collected sufficient, in the opinion of the experimentalist, for reduction, it may be thrown upon a filter, washed thoroughly with hot water and afterwards dried; when dry it must be detached from the filter, and the filter must then be burnt until all the carbonaceous matter of the filter is destroyed; the filter ash along with the silver it may contain may be added to the silver salt or placed in the silver residue bottle. The silver may be obtained from the dried AgCl by one or other of the following processes:—(1) Mix it with twice its weight of reagent 34 (page 405), and then introduce the mixture into a Cornish clay crucible, which it ought only to half fill, and afterwards place the crucible in a furnace and raise the heat gradually until the mixture becomes fluid, keep it in that state for about five minutes, and then remove the crucible from the furnace, tap it slightly on the bottom two or three times so as to cause all the particles of silver to collect together in a mass, and then allow it to cool; when cold, the crucible is broken and the silver, which has collected in the form of a button if the operation has been well performed, is removed and freed by washing from any adhering particles of the alkaline salts. This process succeeds with experienced chemists, but often fails with beginners, for the heat must be gradually applied and the crucible not more than half full, otherwise the effervescence caused by the evolution of CO_2 and O may cause a loss of the substance; and the heat finally must be high enough, otherwise the silver remains disseminated through the mass of the alkaline salts; and yet it must not be too high, otherwise the crucible is corroded and the silver flows into the fire. In order to obviate these disadvantages, the late Professor Gregory recommended the *undried* AgCl to be boiled with a very strong solution of caustic potash, till it is entirely or in great part converted into black oxide of silver; this is then collected, washed thoroughly, then dried, and, finally, fused with a little potassic carbonate and borax, which yields a button of silver without any risk. If all the AgCl was converted into Ag_2O by boiling with KHO, simple ignition would be sufficient to obtain the silver in the metallic state. (2) Boil 6 parts of silver chloride for half an hour with 9 parts of a solution of caustic soda of 1·333 sp. gr., 1½ parts of clarified honey, and 8 parts of water; when the heat is withdrawn let the finely divided silver collect at the bottom of the vessel, and then pour off the liquid and wash the silver thoroughly by decantation. (3) The AgCl is placed in contact with iron or zinc and water, to which, in order to accelerate the action, a small quantity of HCl or H_2SO_4 may be added; the reduced silver must be quickly washed first with acidulated and afterwards with hot pure water, and then fused with borax and nitre. Convert the metallic silver obtained by any of these different processes into nitrate as directed at 51, (page 408).

APPENDIX B. TREATMENT OF PLATINUM RESIDUES.—Platinum residues are collected in a bottle, and when a sufficient quantity has collected the mixture, the liquid and precipitate, is evaporated to dryness in a porcelain dish, and ignited so as to decompose the platinic salts, and the residue washed to remove the soluble matter; a small quantity of oxalic acid in solution is then added to it, and the mixture is again evaporated and ignited so as to decompose any $PtCl_4, 2KCl$, which may have escaped decomposition on the first ignition; the ignited mass is again thoroughly washed with hot water, it must then be boiled in dilute HCl and the insoluble portion again washed thoroughly with hot water; it is then converted into $PtCl_4$ as directed at 54 (page 408). If the dry $PtCl_4$ does not dissolve completely in spirits of wine it must be redissolved in water, and a saturated solution of NH_4Cl added to it, the precipitated $PtCl_4, 2NH_4Cl$ must be collected upon a filter, washed first with a little water, and, finally, with methylated spirit and ignited; the spongy platinum thus obtained must be converted into $PtCl_4$ as directed at 54 (page 408).

APPENDIX C. TREATMENT OF GOLD RESIDUES.—Gold residues are collected in a bottle, and when a sufficient quantity has collected the mixture is evaporated to dryness and ignited. The ignited mass is washed thoroughly with hot water, and the insoluble matter is dissolved in aqua regia; evaporate to dryness over the water-bath; redissolve the residue in water; mix it with an excess of saturated solution of oxalic acid and boil for some time; finally, free by washing the spongy mass of gold from foreign matter, and then convert it into $AuCl_3$, as directed at 55 (page 409).

Fig 4.

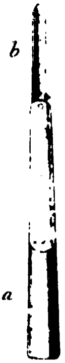


Fig 1.

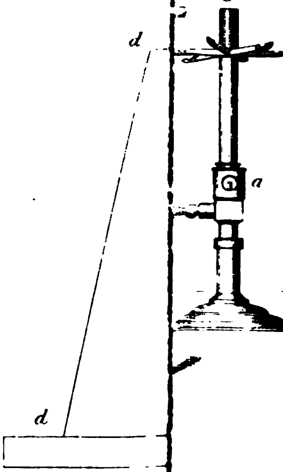
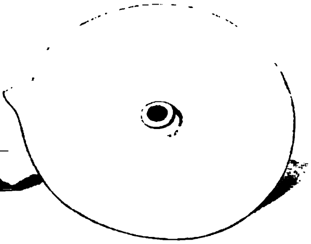


Fig 3.



INDEX.

PAGE
Acetates, properties of 228
Acetic acid as reagent 399
„ behaviour of, with reagents 228
„ detection of 235
„ properties of 228
Acids, classification of 171
„ organic, classification of 232
„ of the bile in calculi 337
„ volatile inorganic, behaviour of salts of, with sulphuric acid . 216
Action of water on lead 147
Albumen, behaviour of, with reagents 295
„ composition of 292
„ detection of 303
„ examination for 327
„ properties of 289, 338
„ varieties of 298
Albumenoids, Gerhardt's views on the constitution of . . . 293
„ Mulder's „ . . . 293
„ Strecker's „ . . . 294
Albumenoid substances 289
Alcohol, conversion into acetic acid 228
Alkaloids, poisonous, detection of, in organic mixtures . . . 363
Aluminic chloride, properties of 64
„ compounds, blowpipe test for 68
„ „ characteristic tests for 68
„ „ properties of 67
„ nitrate, „ 65
„ oxide, „ 62
„ phosphate, „ 74
„ sulphate, „ 65
„ sulphide, „ 64
Aluminum, properties of 61, 67
Ammonia as reagent 401
„ examination for 11, 18
„ Nessler's test for 19
„ properties of 15
Ammonic arseniate as reagent 402
„ carbonate „ 401
„ chloride „ 401

PAGE
Ammonic chloride, properties of 16
„ compounds, characteristic tests for 19
„ „ properties of 18
„ „ special tests for 18
„ hydrate, properties of 15
„ molybdate as reagent 402
„ nitrate „ 401
„ oxalate „ 401
„ oxide 9
„ sulphate, properties of 17
„ sulphide as reagent 401
„ sulphocyanide as reagent 403
„ urate in calculi 336
Ammonio-nitrate of silver as reagent 408
„ sulphate of copper „ 408
Ammonium, compounds of 15, 18
Analysis of animal secretions 326
„ „ substances 289
„ calculi 335
„ ash of organic substances 284
„ organic substances 279
„ solids insoluble in acids 271
„ „ soluble „ 270
„ „ „ in water 270
„ urine 289, 331
„ first basic group 11
„ „ precautions 12
„ second basic group 26
„ „ „ Fresenius's method 36
„ „ „ photo-chemical „ 37
„ „ „ precautions 29
„ third basic group 41
„ „ „ precautions 45
„ fourth basic group, first method 59
„ „ „ second „ 61
„ „ „ third „ 61
„ „ „ containing phosphates and oxalates . 77
„ fifth basic group, first method 85
„ „ „ second „ 85
„ „ „ third „ 86
„ „ „ fourth „ 86
„ „ „ fifth „ 86
„ „ „ sixth „ 87
„ sixth basic group 126
„ „ „ precautions 131
„ first group inorganic acids 209
„ second „ „ 209
„ third „ „ 210
„ fourth „ „ 212
„ first „ organic acids 233
„ second „ „ 233
„ third „ „ 233
„ fourth „ „ 234
Animal secretions, analysis of 326

PAGE
Animal substances, behaviour of, with reagents . 291
„ „ distillation of . 290
„ „ oxidation of . 290
„ „ proximate analysis of . 289
Antimonious chloride, properties of . 94
„ hydrate, „ . 101
„ oxide, „ . 90
„ salts, „ . 100
„ sulphide, „ . 91
Antimonuretted hydrogen, „ . 98
Antimony compounds, blowpipe tests for . 106
„ „ characteristic tests for . 106
„ „ flame reactions . 106
„ „ properties of . 104
„ „ special tests for . 104
„ detection of, in organic mixtures . 105
„ hydride of, properties of . 98
„ properties of 88, 104
Apparatus, list of . 412
Argentic chloride, properties of . 136
„ compounds, blowpipe tests for . 139
„ „ characteristic tests for . 140
„ „ properties of . 138
„ nitrate as reagent . 408
„ „ properties of . 137
„ oxide, „ . 134
„ peroxide . 140
„ salts, properties of . 137
„ suboxide . 140
„ sulphate, properties of . 137
„ sulphide, „ . 135
Arrangement of results . 7
Arseniates, behaviour of, with reagents . 121
„ properties of . 101
Arsenic acid as reagent . 402
„ behaviour of, with reagents . 121
„ characteristic tests for . 212
„ properties of . 101
Arsenic anhydride, „ . 90
„ compounds flame reactions . 121
„ „ properties of . 107
„ „ special tests for . 108
„ detection of, by electrolysis . 118
„ „ in organic mixtures . 115
„ dialytic method for detection of . 115
„ hydride of, properties of . 98
„ Marsh's test for . 111
„ „ „ precautions . 113
„ properties of 88, 107
„ Reinsch's test for . 114
„ sulphide, properties of . 91
Arsenious acid, characteristic tests for . 212
„ properties of . 101
Arsenious anhydride, properties of . 90

PAGE
Arsenious chloride, properties of 94
,, oxide, behaviour of, with reagents 108
,, sulphide, properties of 91
Arsenites, behaviour of, with reagents 109
,, properties of 101
Arsenuretted hydrogen, properties of 98
Ash of organic substances, analysis of 284
,, ,, constituents of 285
Auric chloride as reagent 409
,, ,, properties of 97
,, compounds ,, 122
,, ,, special tests for 122
,, oxide, properties of 90
,, salts, ,, 101
,, sulphide, ,, 91
Aurous oxide, ,, 123

Baric carbonate as reagent 407
,, chloride ,, 406
,, ,, properties of 31
,, compounds, special tests for 34
,, ,, characteristic tests for 34
,, ,, flame reactions 34
,, ,, properties of 34
,, oxide, ,, 30
,, nitrate as reagent 406
,, ,, properties of 32
,, salts, general character of 33
,, sulphate, properties of 32
,, sulphide, ,, 31
Barium, properties of 29, 33
Basic groups, behaviour of, with reagents 160
,, list of 5
Bassorin 348
Behaviour of acetic acid with reagents 228
,, albumen with reagents 295
,, animal substances ,, 291
,, arseniates ,, 121
,, arsenic acid ,, 121
,, arsenious oxide ,, 108
,, arsenites ,, 109
,, basic groups with group reagents 160
,, benzoic acid with reagents 225
,, bilirubine ,, 324
,, boracic acid ,, 176
,, brucine ,, 360
,, calculi on heating 336
,, cane-sugar with reagents 344
,, carbonic acid ,, 183
,, casein ,, 301
,, cellulose ,, 340
,, chloric acid ,, 207
,, cholepyrrhin ,, 324
,, cholestrin ,, 323

PAGE
Behaviour of chondrin with reagents 307
„ chromic acid „ 172
„ cinchonine „ 356
„ citric acid „ 222
„ creatin „ 317
„ creatinine „ 316
„ cystine „ 321
„ elements at high temperatures . . . 384
„ fibrin with reagents 300
„ first basic group with special reagents . . 10
„ formic acid with reagents . . . 229
„ fourth basic group with special reagents . . 60
„ gallic acid with reagents . . . 227
„ gelatin „ . . . 305
„ glucose „ . . . 309
„ glutin „ . . . 305
„ glyco-cholalic acid with reagents . . . 319
„ grape sugar „ . . . 309
„ gum „ . . . 343
„ hippuric acid „ . . . 318
„ hydriodic acid „ . . . 195
„ hydrobromic acid „ . . . 197
„ hydrochloric acid „ . . . 193
„ hydrocyanic acid „ . . . 200
„ hydrofluoric acid „ . . . 189
„ hydrosulphuric acid „ . . . 191
„ hyposulphurous acid „ . . . 176
„ inosite „ . . . 312
„ iodic acid „ . . . 197
„ lactic acid „ . . . 317
„ lignin „ . . . 340
„ malic acid „ . . . 224
„ meconic acid „ . . . 361
„ metaphosphoric acid „ . . . 182
„ milk sugar „ . . . 309
„ morphine „ . . . 349
„ narcotine „ . . . 352
„ nicotine „ . . . 347
„ nitric acid with metals . . . 276
„ „ with reagents . . . 203
„ oxalic acid „ . . . 185
„ phaseomannite „ . . . 312
„ phosphoric acid „ . . . 178
„ pyrophosphoric acid „ . . . 182
„ quinine „ . . . 354
„ salts of volatile inorganic acids with sulphuric acid . 216
„ second basic group with special reagents . . 27
„ silicic acid with reagents . . . 186
„ sixth basic group with special reagents . . 128
„ starch with reagents 342
„ strychnine „ 357
„ succinic acid „ 226
„ sugar of milk „ 309

PAGE
Behaviour of sulphuric acid with reagents . . . 174
„ sulphurous acid „ . . . 176
„ tannic acid „ . . . 227
„ tartaric acid „ . . . 219
„ taurocholalic acid „ . . . 321
„ taurocholic acid „ . . . 321
„ thiosulphuric acid „ . . . 176
„ third basic group with special reagents . . 42
„ titanic oxide with reagents . . . 83
„ uranic oxide „ . . . 82
„ urea „ 313
„ uric acid „ 231
„ xanthine „ 323
Benzamidacetic acid, behaviour of, with reagents . . 318
„ composition of 318
„ properties of 318
Benzoic acid, behaviour of, with reagents . . . 225
„ detection of 234
Bile acids, examination for 330
„ colouring matter, examination for . . . 330
„ colouring matter of 324
„ in urine 333
„ Pettenkofer's test for 320, 326
„ properties of 325
„ tests for 325
Bilirubine, behaviour of, with reagents . . . 324
„ composition of 324
„ detection of 324
„ properties of 324
Biliverdine „ 324
Binoxide of lead 150
Bismuth compounds, blowpipe test for . . . 145
„ „ characteristic tests . . . 145
„ „ flame reactions 145
„ „ properties of 144
Bismuthic anhydride 145
„ dioxide 145
Bismuthous chloride, properties of 136
„ nitrate, „ 137
„ oxide, „ 134
„ salts, „ 137
„ sulphide, „ 135
Bismuth „ 132, 144
Blood, colouring matter of 324
„ tests for 325
Blowpipe 374
„ operations 242
„ „ supports for 376
„ test for aluminic compounds 68
„ „ antimony „ 106
„ „ argentic „ 139
„ „ bismuth „ 145
„ „ bromides 199
„ „ chlorides 194

PAGE
Blowpipe test for chromic compounds 69
„ „ cobalt „ 55
„ „ cupric „ 152
„ „ iodides 196
„ „ lead 149
„ „ manganese 50
„ „ nickel compounds 53
„ „ silicic acid 189
„ „ sulphates 175
„ „ tin compounds 103
„ „ zincic „ 52
Boracic acid, behaviour of, with reagents . . . 176
„ characteristic tests for 212
Borax as reagent 405
Brazil wood paper 412
Bromides, blowpipe test for 199
Bromine, detection of, in presence of iodine and chlorine . . 199
Brucine, behaviour of, with reagents . . . 360
„ composition of 360
„ properties of 360
Bunsen's flame reactions 268
„ gas lamp 382

Cadmic chloride, properties of 136
„ nitrate, „ 137
„ oxide, „ 134
„ salts, „ 137
„ sulphide, „ 135
Cadmium and copper, separation of 153
„ compounds, blowpipe tests for . . . 146
„ „ flame reactions 146
„ „ properties of 146
„ properties of 132, 146
Calcic carbonate in calculi 338
„ chloride as reagent 407
„ „ properties of 31
„ compounds, characteristic tests for . . . 36
„ „ flame reactions 36
„ „ properties of 35
„ „ special tests for 35
„ nitrate, properties of 32
„ oxalate, detection of 76
„ „ in calculi 337
„ oxide, properties of 32
„ phosphate, detection of 76
„ „ in calculi 337
„ salts, general character of 33
„ sulphate as reagent 407
„ „ properties of 32
„ sulphide „ 31
„ urate in calculi 338
Calcium, properties of 29, 35
Calculi, analysis of 335
„ behaviour of, on heating 336

PAGE
Calculi, classification of 335
„ composition of 335
„ containing ammonic urate 336
„ „ cholesterine 336
„ „ cystine 336
„ „ fibrin 336
„ „ uric acid 336
„ „ xanthine 336
Cane-sugar, behaviour of, with reagents . . . 344
„ composition of 344
„ properties of 344
Caramel 345
Carbonates, properties of 183
Carbonic acid, behaviour of, with reagents . . . 183
„ „ characteristic tests for . . . 213
„ „ precautions in examining for . . . 184
Casein, behaviour of, with reagents 301
„ composition of 292
„ detection of 304
„ examination for 328
„ properties of 289, 301, 339
Cellulose, behaviour of, with reagents 340
„ composition of 340
„ properties of 340
Characteristic reagents 2
„ tests for aluminic compounds . . . 68
„ „ ammonic „ . . . 19
„ „ antimony „ . . . 106
„ „ agentic „ . . . 140
„ „ arsenic acid 212
„ „ arsenious acid 212
„ „ baric compounds . . . 34
„ „ bismuth „ . . . 145
„ „ boracic acid 212
„ „ calcic compounds . . . 36
„ „ carbonic acid 213
„ „ chloric acid 214
„ „ chromic acid 212
„ „ „ compounds . . . 69
„ „ cobalt „ . . . 56
„ „ cupric „ . . . 152
„ „ ferric „ . . . 71
„ „ ferrous „ . . . 71
„ „ hydriodic acid 214
„ „ hydrochloric acid . . . 213
„ „ hydrocyanic acid . . . 214
„ „ hydrofluoric acid . . . 213
„ „ hydrosulphuric acid . . . 213
„ „ lead compounds . . . 150
„ „ lithic „ . . . 24
„ „ magnesic compounds . . . 39
„ „ manganese „ . . . 51
„ „ mercury „ . . . 144

PAGE
Characteristic tests for nickel compounds . . . 54
„ „ nitric acid 214
„ „ oxalic acid 213
„ „ phosphoric acid . . . 212
„ „ potassic compounds . . . 22
„ „ silicic acid 213
„ „ sodic compounds . . . 23
„ „ strontic „ . . . 35
„ „ sulphuric acid . . . 212
„ „ uranium compounds . . . 82
„ „ zincic „ . . . 52
Chlorates, properties of 207
Chloric acid, behaviour of, with reagents . . . 207
„ characteristic tests for 214
Chlorides, blowpipe test for 194
Chlorine as reagent 400
„ detection of 194
Cholepyrrhin, behaviour of, with reagents . . . 334
„ composition of 324
„ detection of 324
„ properties of 324
Cholestrin, behaviour of, with reagents . . . 223
„ composition of 323
„ in calculi 336
„ properties of 323
Chondrin, behaviour of, with reagents . . . 307
„ composition of 305
„ detection of 305, 308
„ examination for 328
„ oxidation of 305
„ properties of 304
Chromates, „ 172
Chromic acid, behaviour of, with reagents . . . 172
„ „ characteristic tests for . . . 212
„ anhydride, properties of 172
„ chloride, „ 64
„ compounds, blowpipe tests for . . . 69
„ „ characteristic tests for . . . 69
„ „ properties of 68
„ „ special tests for 69
„ oxide, properties of 62
„ phosphate, „ 75
„ nitrate, „ 65
„ sulphate, „ 65
„ sulphide, „ 64
Chromium, properties of 61, 68
Cinchonine, behaviour of, with reagents . . . 356
„ composition of 356
„ properties of 356
Citrates, properties of 222
Citric acid, behaviour of, with reagents . . . 222
„ detection of 234
„ preparation of 222

PAGE
Classification of acids 171
„ calculi 335
„ inorganic acids 209
„ organic acids 232
Coagulation of milk 302
Cobalt compounds, blowpipe tests for 55
„ characteristic tests for . . . 56
„ flame reactions 55
„ properties of 54
„ special tests for 54
Cobaltic nitrate as reagent 408
Cobaltous chloride, properties of 47
„ nitrate, „ 48
„ oxide, „ 46
„ salts, „ 49
„ sulphate, „ 48
„ sulphide, „ 47
Cobalt, „ 45, 54
Coloration of flame 243
Colouring matter of the bile 324
„ „ examination for . . . 330
„ „ in calculi . . . 337
„ „ blood 324
„ „ urine 324
Composition of albumen 292
„ bilirubine 324
„ brucine 360
„ calculi 335
„ cane-sugar 344
„ casein 292
„ cellulose 340
„ cholepyrrhin 324
„ cholestrin 323
„ chondrin 305
„ cinchonine 356
„ creatin 317
„ creatinine 316
„ cystine 321
„ fibrin 292
„ gelatin 305
„ glucose 309
„ glyco-cholalic acid 319
„ grape-sugar 309
„ gum 343
„ hippuric acid 318
„ inosite 312
„ lactic acid 317
„ lactin 309
„ lactose 309
„ lignin 340
„ meconic acid 361
„ milk-sugar 309
„ morphine 349
„ narcotine 352
„ nicotine 347

PAGE
Composition of phaseomannite 312
„ quinine 354
„ silicates 188
„ starch 342
„ strychnine 357
„ sugar of milk 309
„ taurocholalic acid 321
„ taurocholic acid 321
„ urea 313
„ urine 331
„ xanthine 323
Constituents of ash of organic substances . . . 285
Constitution of the albumenoids, Strecker's views . . 294
„ „ Gerhardt's „ . . 293
„ „ Mulder's „ . . 293
Conversion of alcohol into acetic acid 228
Copper and cadmium, separation of 153
„ detection of, in organic liquids . . . 151
„ „ solids . . . 152
„ properties of 132, 150
„ turnings as reagent 409
Creatine, behaviour of, with reagents 317
„ composition of 317
„ examination for 330
„ properties of 317
Creatinine, behaviour of, with reagents . . . 316
„ composition of 316
„ detection of 316
„ examination for 330
„ properties of 316
Cupellation 260
Cupric chloride, properties of 136
„ compounds, blowpipe test for 152
„ „ characteristic tests for . . . 152
„ „ flame reactions 152
„ „ properties of 150
„ nitrate, „ 137
„ oxide, „ 134
„ salts, „ 137
„ sulphate as reagent 408
„ sulphide, properties of 135
Cystine, behaviour of, with reagents 321
„ composition of 321
„ detection of 322
„ in calculi 336
„ properties of 321

Decantation 371
Deflagration 2, 374
Detection of acetic acid 235
„ albumen 303
„ antimony in organic mixtures . . . 105
„ arsenic by dialytic method . . . 115
„ „ by electrolysis 118
„ „ in organic mixtures . . . 115

PAGE
Detection of benzoic acid . . 234
„ bilirubine . . 324
„ bromine in presence of iodine and chlorine . . 199
„ casein . . 304
„ cholepyrrhin . . 324
„ chondrin . . 305, 308
„ citric acid . . 234
„ copper in organic liquids . . 151
„ „ solids . . 152
„ creatinine . . 316
„ cystine . . 322
„ fibrin . . 304
„ formic acid . . 235
„ free sulphuric acid in presence of a sulphate . . 175
„ gallic acid . . 235
„ gelatin . . 305, 308
„ glucose . . 310
„ grape-sugar . . 310
„ hydrocyanic acid in mercuric cyanide . . 202
„ „ organic mixtures . . 202
„ iodates in presence of iodides . . 197
„ lead in organic mixtures . . 149
„ „ waters . . 148
„ malic acid . . 234
„ mercury in organic liquids . . 142
„ „ solids . . 142
„ opium in organic mixtures . . 362
„ poisonous alkaloids in organic mixtures . . 363
„ „ metals by electrolysis . . 119
„ strychnine in organic mixtures . . 359
„ succinic acid . . 235
„ sugar . . 311
„ tannic acid . . 235
„ tartaric acid . . 234
„ „ in presence of citric acid . . 223
„ urea . . 315
„ uric acid . . 235
„ xanthine . . 323
Determination of fusibility of solids . . 263
Dialytic method for detection of arsenic . . 115
Dibasic silicic acid, preparation of . . 187
Dihydric dipotassic metantimoniate as reagent . . 406
Disodic hydric phosphate „ . . 405
Distillation . . 372
„ of animal substances . . 290
Distilled water . . 410

Effervescence . . 2
Electrolytic detection of arsenic . . 118
„ „ poisonous metals . . 119
Elements, behaviour of, at high temperatures . . 384
„ flame reactions of . . 393
Emerald green . . 101
Evaporation . . 372

PAGE
Examination for albumen 327
„ ammonia 11
„ bile acids 330
„ casein 328
„ chondrin 328
„ colouring matter of the bile . . . 330
„ creatine 330
„ creatinine 330
„ fatty matter 331
„ globulin 328
„ glucose 330
„ hæmatin 327
„ inorganic acids . . . 214, 239
„ lactic acid 330
„ morphine 352
„ mucus 328
„ nicotine 348
„ nitrogen 281
„ organic acids 235
„ phosphorus in organic substances . . 282
„ potassic compounds 11
„ pus 328
„ sodic compounds 11
„ sulphur in organic substances . . . 282
„ urea 330
„ uric acid 329
Examination of liquids 238
„ solids 241
„ „ with borax 261
„ „ in closed tube 247
„ „ in open tube 254
„ „ on charcoal 256
„ „ „ with cobaltic nitrate . . 256
„ „ „ with sodic carbonate . . 258
Exercises on first basic group 24
„ second „ 39
„ third „ 56
„ fourth „ . . . 72, 81
„ fifth „ 124
„ sixth „ 153
„ all „ 170
„ inorganic acids 217
„ organic acids 237
„ organic alkaloids 367
„ examination of liquids 241
„ „ solids 277
„ animal chemistry 346

Fatty matter, examination for 331
„ in urine 333
Fermentation of glucose 310
„ of grape sugar 310
„ test for sugar 311

PAGE

Ferments 290

Ferric chloride as reagent 407

„ „ properties of 64

„ compounds, characteristic tests for . . . 71

„ nitrate, properties of 65

„ oxide, „ 62

„ phosphate, „ 75

„ sulphate, „ 65

„ sulphide, „ 64

Ferrous chloride, „ 64

„ compounds, characteristic tests for . . . 71

„ oxide, properties of 62

„ sulphate as reagent 407

„ „ properties of 65

„ sulphide 64

Fibrin, behaviour of, with reagents 300

„ composition of 292

„ detection of 304

„ in calculi 336

„ properties of 289, 299, 339

Fifth basic group, analysis of first method . . . 85

„ „ second „ . . . 85

„ „ third „ . . . 86

„ „ fourth „ . . . 86

„ „ fifth „ . . . 86

„ „ sixth „ . . . 87

„ precautions in examining for . . 166

„ precipitation of . . . 157

Films of volatile elements 266, 390

Filtration 371

First basic group, analysis of 11

„ „ behaviour of, with special reagents . . 10

„ „ examination for 163

„ „ precautions in analysis of . . . 12

„ „ properties of 9

First group of inorganic acids, analysis of . . . 209

„ organic „ „ . . . 233

Flame coloration 243, 387

Flame reactions 268

„ of antimony compounds . . . 106

„ arsenic „ . . . 121

„ baric „ . . . 34

„ bismuth „ . . . 145

„ cadmium „ . . . 146

„ calcic „ . . . 36

„ cobalt „ . . . 55

„ cupric „ . . . 152

„ iron „ . . . 71

„ lead „ . . . 149

„ lithic „ . . . 23

„ mercury „ . . . 143

„ nickel „ . . . 53

„ potassic „ . . 11, 20

„ sodic „ . . . 22

PAGE
Flame reactions of strontic compounds . . . 35
„ tin „ . . . 103
„ titanic „ . . . 84
„ uranium „ . . . 82
„ zincic „ . . . 52
„ elements 393
Formates, properties of 230
Formation of precipitates 2
Formic acid, behaviour of, with reagents . . . 229
„ detection of 235
„ preparation of 230
Fourth basic group, analysis of first method . . . 59
„ „ second „ . . . 61
„ „ third „ . . . 61
„ behaviour of, with special reagents . . 60
„ precautions in analysis of . . . 76
„ „ in examining for . . 167
„ precipitation of 159
Fourth group of inorganic acids, analysis of . . . 212
„ organic „ „ . . . 234
Fowler's solution 101
Fresenius's method of analysis of second basic group . . 36
Fusibility of solids, determination of 263
Fusible calculus 337
Fusion 373
„ of solids by deflagration 272

Gallic acid, behaviour of, with reagents . . . 227
„ „ detection of 235
„ and tannic acids, separation of . . . 227
Gelatigenous substances 304
Gelatine, behaviour of, with reagents 305
„ composition of 305
„ detection of 305, 308
„ oxidation of 305
„ properties of 304
General characters of aluminic salts 66
„ ammonic „ 17
„ antimony „ 99
„ argentic „ 137
„ arsenic „ 99
„ auric „ 99
„ baric „ 33
„ bismuthic „ 137
„ cadmic „ 137
„ calcic „ 33
„ chromic „ 66
„ cobaltous „ 49
„ cupric „ 137
„ ferric „ 66
„ ferrous „ 66
„ lithic „ 17
„ magnesic „ 33

PAGE

General characters of manganous salts . . . 49
,, mercuric ,, . . . 137
,, mercurous ,, . . . 137
,, nickelous ,, . . . 49
,, platinic ,, . . . 99
,, plumbic ,, . . . 137
,, potassic ,, . . . 17
,, sodic ,, . . . 17
,, stannic ,, . . . 99
,, stannous ,, . . . 99
,, strontic ,, . . . 33
,, zincic ,, . . . 49
Gerhardt's views on the constitution of the albumenoids . . 293
Globulin, examination for 328
,, properties of 302
Glucose, behaviour of, with reagents 309
,, composition of 309
,, detection of 310
,, examination for 330
,, fermentation of 310
,, properties of 309
Gluten, ,, ... 339
Glutin, behaviour of, with reagents 305
Glyco-cholalic acid, behaviour of, with reagents . . 319
,, composition of 319
,, properties of 319
Glycocholic acid, behaviour of, with reagents . . . 319
,, composition of 319
,, properties of 319
Glyco-hyocholic acid, behaviour of, with reagents . . 320
,, composition of 320
,, properties of 320
Gold, properties of 88, 122
,, residues, treatment of 415
Grape-sugar, behaviour of, with reagents . . . 309
,, composition of 309
,, detection of 310
,, fermentation of 310
,, properties of 309
Group reagents 2
,, behaviour of basic groups with . . . 160
Gum, behaviour of, with reagents 343
,, composition of 343
,, properties of 343

Hæmatin, examination for 327
,, properties of 324
Hippuric acid, behaviour of, with reagents . . . 318
,, composition of 318
,, properties of 318
How the book ought to be studied 3
Hydric peroxide, preparation of 173
Hydride of antimony, properties of 98

PAGE
Hydride of arsenic, properties of 98
Hydriodic acid, behaviour of, with reagents 195
„ characteristic tests for 214
Hydrobromic acid, behaviour of, with reagents 197
Hydrochloric acid as reagent 396
„ behaviour of, with reagents 193
„ characteristic tests for 213
Hydrocyanic acid, behaviour of, with reagents 200
„ characteristic tests for 214
„ detection of, in mercuric cyanide 202
„ „ in organic mixtures 202
„ test-papers for 412
Hydrofluosilicic acid as reagent 400
Hydrofluoric acid, behaviour of, with reagents 189
„ characteristic tests for 213
Hydrosulphuric acid as reagent 399
„ behaviour of, with reagents 191
„ characteristic tests for 213
Hyposulphurous acid, behaviour of, with reagents 176

Indigo, solution of, as reagent 410
Ignition 373
Imperfect precipitation 6
Inorganic acids, classification of 209
„ examination for 214
„ first group of, analysis of 209
„ second „ „ 209
„ third „ „ 210
„ fourth „ „ 212
Inosite, behaviour of, with reagents 312
„ composition of 312
„ properties of 312
Iodates, detection of, in presence of iodides 197
Iodic acid, behaviour of, with reagents 197
Iodides, blowpipe test for 196
Iodine, detection of 195, 196
Iron compounds, flame reactions 71
„ „ properties of 70
„ „ special tests for 70
„ liquor 228
„ properties of 61, 70

Lactic acid, behaviour of, with reagents 317
„ composition of 317
„ examination for 330
„ properties of 317
Lactin, behaviour of, with reagents 309
„ composition of 309
„ properties of 309
Lactose, behaviour of, with reagents 309
„ composition of 309
„ properties of 309
Lead, action of water on 147

PAGE
Lead binoxide 147
„ compounds, blowpipe test for 149
„ „ characteristic tests for 150
„ „ flame reactions 149
„ detection of, in organic mixtures 149
„ „ waters 148
„ properties of 132, 147
„ suboxide 150
Legumine, properties of 339
Lignin, behaviour of, with reagents 340
„ composition of 340
„ properties of 340
Lime water as reagent 407
List of apparatus 412
Litharge 147
Lithic chloride, properties of 16
„ compounds, characteristic tests for 24
„ „ flame reactions 23
„ „ properties of 23
„ „ special tests for 23
„ hydrate, preparation of 14
„ oxide, properties of 9, 13
Lithium, properties of 13
Litmus papers, preparation of 411

Magnesic ammonic phosphate in calculi 337
„ chloride, properties of 31
„ compounds, characteristic tests for 39
„ „ properties of 37
„ „ special tests for 38
„ nitrate, properties of 32
„ oxide, „ 30
„ salts, general character of 33
„ sulphate as reagent 407
„ „ properties of 32
„ sulphide, „ 31
„ urate in calculi 338
Magnesium, properties of 29, 37
Malates, „ 224
Malic acid, behaviour of, with reagents 224
„ detection of 234
Manganese, blowpipe test for 50
„ compounds, characteristic tests for 51
„ „ properties of 50
„ „ special tests for 50
„ properties of 45, 50
Manganous chloride, properties of 47
„ nitrate, „ 48
„ oxide, „ 46
„ salts, „ 49
„ sulphate, „ 48
„ sulphide, „ 47
Marsh's test for arsenic 111

PAGE
Marsh's test for arsenic, precautions 113
Massicot 147
Meconic acid, behaviour of, with reagents . . . 361
„ composition of 361
„ properties of 361
Melassic acid 310
Melting-point of substances 387
Mercuric chloride as reagent 408
„ „ properties of 136
„ nitrate, „ 137
„ oxide, „ 134
„ salts, „ 137
„ sulphide, „ 135
Mercurous chloride „ 136
„ nitrate as reagent 407
„ „ properties of 137
„ oxide, „ 134
„ salts, „ 137
„ sulphate, „ 137
„ sulphide, „ 135
Mercury compounds, characteristic tests for . . . 144
„ „ flame reactions 143
„ „ properties of 140
„ „ special tests for 141
„ detection of, in organic liquids . . . 142
„ „ solids . . . 142
„ properties of 132, 140
Metalbumin 299
Metals of first basic group 18
Metaphosphoric acid, behaviour of, with reagents . . 182
Metastannic hydrate, properties of 100
Microcosmic salt as reagent 405
Milk, coagulation of 302
Milk-sugar, behaviour of, with reagents . . . 309
„ composition of 309
„ properties of 309
Morphine, behaviour of, with reagents . . . 349
„ composition of 349
„ examination for 352
„ properties of 349
Mucus, examination for 328
Mulder's views on the constitution of the albumenoids . . 293

Narcotine, behaviour of, with reagents . . . 352
„ composition of 352
„ examination for 348
„ properties of 352
Nessler's test for ammonia 19
„ „ preparation of . . . 409
Nickel compounds, blowpipe test for 53
„ characteristic tests for . . . 54
„ flame reactions 53
„ properties of 53

PAGE
Nickel, properties of 45, 52
Nickelous chloride, properties of 47
,, nitrate, ,, ... 48
,, oxide, ,, ... 46
,, salts, ,, ... 49
,, sulphate, ,, ... 48
,, sulphide, ,, ... 47
Nicotine, behaviour of, with reagents . . . 347
,, composition of 347
,, properties of 347
Nitrates of first basic group 13
,, properties of 203, 207
Nitric acid as reagent 397
,, behaviour of, with metals 276
,, ,, reagents . . . 203
,, characteristic tests for 214
Nitrogen, examination for 281
Nitro-hydrochloric acid as reagent 397

Opium, detection of, in organic mixtures . . . 362
Organic acids 219
,, classification of 232
,, preliminary examination for . . . 236
,, examination for 235
,, analysis of first group of . . . 233
,, ,, second ,, . . . 233
,, ,, third ,, . . . 233
,, ,, fourth ,, . . . 234
Organic substances, analysis of ash of 284
,, constituents of ash of . . . 285
,, analysis of 279
,, proximate analysis of . . . 283
Oxalates, properties of 76, 185
Oxalic acid as reagent 401
,, behaviour of, with reagents . . . 185
,, characteristic tests for 213
Oxidation of animal substances 290
,, chondrin 305
,, gelatin 305
,, substances 388
Oxides of first basic group 13

Paralbumin 299
Pettenkofer's test for bile 320, 326
Phaseomannite, behaviour of, with reagents . . . 312
,, composition of 312
,, properties of 312
Phenomena accompanying chemical change . . . 2
Phosphates, properties of 74, 179
Phosphoric acid, behaviour of, with reagents . . . 178
,, ,, characteristic tests for . . . 212
,, ,, separation of, from alkaline earths . . 180
,, anhydride, preparation of . . . 179
Phosphorus, detection of 181

PAGE
Phosphorus, examination for, in organic substances . . 282
Photo-chemical method of analysis of second basic group . . 37
Photo-chemistry 394
Plate of apparatus for Bunsen's flame reactions . . . 416
Platinic chloride as reagent 408
„ „ properties of 97
„ compounds, „ 123
„ „ special tests for 123
„ oxide, properties of 90
„ salts, „ 101
„ sulphide, „ 91
Platinous oxide 124
Platinum, properties of 88, 123
„ residues, treatment of 414
Plumbic acetate as reagent 407
„ chloride, properties of 136
„ compounds, „ 147
„ nitrate, „ 137
„ oxide, „ 134
„ peroxide as reagent 409
„ salts, properties of 137
„ sulphate, „ 137
„ sulphide, „ 135
Poisonous metals, detection of, by electrolysis . . . 119
Polysulphides, properties of 16, 192
Potassic antimonious tartrate, preparation of . . . 101
„ arsenite 101
„ chloride, properties of 16
„ chromate as reagent 404
„ compounds, characteristic tests for . . . 22
„ „ examination for 11
„ „ flame reactions 20
„ „ properties of 19
„ „ special tests for 19
„ cyanide as reagent 404
„ ferricyanide „ 403
„ ferrocyanide „ 402
„ hydrate, preparation of 14
„ nitrate, properties of 17
„ nitrite as reagent 402
„ oxide, properties of 18
„ sulphate as reagent 402
„ „ properties of 17
„ sulphide, preparation of 16
„ urate in calculi 338
Potassium, properties of 13, 19
Precautions in analysis of first basic group . . . 12
„ „ second „ . . . 29
„ „ third „ . . . 45
„ „ fourth „ . . . 76
„ „ fifth „ . . . 166
„ „ sixth „ . . . 181
„ in examining for carbonic acid . . . 184
„ „ first basic group . . . 12

PAGE
Precautions in examining for second basic group . . 169
,, ,, third ,, . . . 168
,, ,, fourth ,, . . . 167
,, ,, fifth ,, . . . 166
,, ,, sixth ,, . . . 164
Precipitation 369
,, of second basic group 162
,, third ,, ... 159
,, fourth ,, ... 159
,, fifth ,, ... 157
,, sixth ,, ... 157
Preliminary examination for organic acids 236
Preparation of blue litmus paper 411
,, reddened litmus paper 411
,, Nessler's test for ammonia . . . 409
,, turmeric paper 411
Proteic substances 289
Protein 293
Proximate analysis of animal substances . . . 289
,, organic ,, . . . 283
Pus, examination for 328
Pyroligneous acid 228
Pyrophosphoric acid, behaviour of, with reagents . . 182
Properties of albumen 289, 294, 338
,, bile 325
,, bilirubine 324
,, biliverdine 324
,, brucine 360
,, cane-sugar 344
,, casein 289, 301, 339
,, cellulose 340
,, cholepyrrhin 324
,, cholestrin 323
,, chondrin 304
,, cinchonine 356
,, creatin 317
,, creatinine 316
,, cystine 321
,, fibrin 289, 299, 339
,, gelatin 304
,, globulin 302
,, glucose 309
,, gluten 339
,, glycocholalic acid 319
,, grape-sugar 309
,, gum 343
,, hæmatin 324
,, hippuric acid 318
,, inosite 312
,, lactic acid 317
,, legumine 339
,, lignin 340
,, meconic acid 361

PAGE
Properties of milk-sugar . . . 309
„ morphine . . . 349
„ narcotine . . . 352
„ nicotine . . . 347
„ phaseomannite . . . 312
„ quinine . . . 354
„ starch . . . 342
„ strychnine . . . 357
„ sugar of milk . . . 309
„ taurocholalic acid . . . 321
„ taurocholic acid . . . 321
„ urea . . . 313
„ vitellin . . . 303
„ xanthine . . . 323

Quinine, behaviour of, with reagents . . . 354
„ composition of . . . 354
„ properties of . . . 354
„ test for . . . 355

Reactions . . . 2
Reagent papers . . . 411
Reagents . . . 2
„ characteristic . . . 2
„ group . . . 2
„ special . . . 2
Red lead . . . 150
„ liquor . . . 228
Reduction of substances . . . 388
Reinsch's test for arsenic . . . 114
Residues, treatment of . . . 413

Sarcolactic acid, properties of . . . 318
Scheele's green . . . 101
Schweinfurt green . . . 101
Second basic group, analysis of . . . 26
„ „ behaviour of, with special reagents . . . 27
„ „ Fresenius's method of analysis of . . . 86
„ „ precautions in analysis of . . . 29
„ „ photo-chemical method of analysis of . . . 37
„ „ precautions in examining for . . . 169
„ „ precipitation of . . . 162
„ group of inorganic acids, analysis of . . . 209
„ „ organic „ „ . . . 233
Sediments in urine . . . 334
Separation of copper and cadmium . . . 153
„ phosphoric acid from the alkaline earths . . . 180
„ tannic and gallic acids . . . 227
Silicates, composition of . . . 188
Silicic acid, behaviour of, with reagents . . . 186
„ blowpipe test for . . . 189
„ characteristic tests for . . . 213
„ dibasic, preparation of . . . 187

PAGE
Silicic anhydride, properties of 187
Silver, properties of 132, 138
„ residues, treatment of 413
„ salts, colours of 211
Sixth basic group, analysis of 126
„ „ precautions 131
„ precautions in examining for . . . 164
„ precipitation of 157
„ exercises on 153
Sodic ammonic hydric phosphate as reagent . . . 405
„ and potassic carbonate „ 405
„ acetate 405
„ carbonate 405
„ chloride, properties of 16
„ compounds, characteristic tests for . . . 23
„ „ examination for 11
„ „ flame reactions 22
„ „ properties of 22
„ „ special tests for 22
„ hydrate as reagent 404
„ „ preparation of 14
„ hydric sulphate as reagent 405
„ „ tartrate „ 399
„ nitrate, properties of 17
„ oxide, „ 13
„ sulphate, „ 17
„ sulphide, preparation of 16
„ urate in calculi 338
Sodium, properties of 13
Solids, determination of fusibility of 263
„ insoluble in acids, analysis of 271
„ soluble „ „ 270
„ „ in water, „ 270
Solution 368
„ of indigo as reagent 410
Sources of error 6
Special reagents 2
„ tests for ammonic compounds 18
„ „ antimony „ 104
„ „ auric „ 122
„ „ baric „ 34
„ „ calcic „ 35
„ „ chromic „ 69
„ „ cobalt „ 54
„ „ iron „ 70
„ „ lithic „ 23
„ „ magnesic „ 38
„ „ manganese „ 50
„ „ potassic „ 19
„ „ sodic „ 22
„ „ strontic „ 35
„ „ tin „ 102
„ „ zincic „ 52

PAGE
Stannic chloride, properties of 94
„ hydrate, „ 99
„ oxide, „ 90
„ salts, „ 101
„ sulphide, „ 91
Stannous chloride as reagent 409
„ „ properties of 94
„ oxide, „ 90
„ salts, „ 99, 101
„ sulphide, „ 91
Starch, behaviour of, with reagents 342
„ composition of 342
„ properties of 342
Strecker's views on the constitution of the albumenoids . . 294
Strontic chloride, properties of 31
„ compounds, characteristic tests for 35
„ „ flame reactions 35
„ „ properties of 35
„ „ special tests for 35
„ nitrate, properties of 32
„ oxide, „ 30
„ salts, general characters of 33
„ sulphate, properties of 32
„ sulphide, „ 31
Strontium, properties of 29, 35
Strychnine, behaviour of, with reagents 357
„ composition of 357
„ detection of 359
„ properties of 357
Sublimation 373
Suboxide of lead 150
Succinates, properties of 226
Succinic acid, behaviour of, with reagents . . . 226
„ detection of 235
Sugar, detection of 311
„ fermentation test for 311
„ in urine 333
„ of milk, behaviour of, with reagents . . . 309
„ „ composition of 309
„ „ properties of 309
„ Trommer's test for 311
Sulphates, blowpipe test for 175
„ of first basic group 13
„ properties of 174
Sulph-hydrates „ 16, 31, 192
Sulphides of first basic group 13
„ properties of 192
Sulphur, detection of 193
„ examination for, in organic substances . . . 282
Sulphuric acid as reagent 398
„ „ behaviour of, with reagents . . . 174
„ „ characteristic tests for 212
„ „ detection of, in presence of a sulphate . . 175

PAGE
Sulphuric anhydride, properties of 174
Sulphurous acid, behaviour of, with reagents 176
,, properties of 175
,, anhydride as reagent 400
Sulphur salts, formation of 92
Supports for blowpipe operations 376

Tannic acid, behaviour of, with reagents 227
,, ,, detection of 235
,, and gallic acids, separation of 227
Tartar emetic, preparation of 101
Tartaric acid as reagent 399
,, behaviour of, with reagents 219
,, detection of 234
,, ,, in presence of citric acid 223
,, preparation of 220
Tartrates, properties of 220
Taurocholalic acid, behaviour of, with reagents 321
,, ,, composition of 321
,, ,, properties of 321
Taurocholic ,, behaviour of, with reagents 321
,, ,, composition of 321
,, ,, properties of 321
Tests 2
,, for bile 325
,, for blood 325
,, for quinine 355
Test-papers for hydrocyanic acid 412
Third basic group, analysis of 41
,, ,, behaviour of, with special reagents 43
,, ,, precautions in analysis of 45
,, ,, ,, in examining for 168
,, ,, precipitation of 159
,, group of inorganic acids, analysis of 210
,, ,, organic ,, ,, 233
Thiosulphuric acid, behaviour of, with reagents 176
Tin compounds, blowpipe test for 103
,, ,, flame reactions 103
,, ,, properties of 102
,, ,, special tests for 102
,, properties of 88, 102
Titanic compounds, flame reactions 84
,, oxide, behaviour of, with reagents 83
,, ,, properties of 82
Treatment of gold residues 415
,, platinum ,, 414
,, silver ,, 413
Trommer's test for sugar 311
Turmeric paper, preparation of 411
Type metal, composition of 104

Uranic oxide, behaviour of, with reagents 82
,, properties of 82

PAGE
Uranium compounds, characteristic tests for . . . 82
„ flame reactions . . . 82
Urates, properties of 231
Urea, behaviour of, with reagents 313
„ composition of 313
„ detection of 315
„ examination for 330
„ properties of 313
Uric acid, behaviour of, with reagents . . . 231
„ detection of 235
„ examination for 329
Uric acid in calculi 336
Urinary sediments 334
Urine, analysis of 289, 331
„ colouring matter of 324
„ composition of 331
„ containing bile 333
„ „ fatty matters 333
„ „ sugar 333
Urochrome 324

Varieties of albumen 298
Vitellin, properties of 303
Volatile elements which can be reduced as films . . 266
Volatility of substances 387

Water, action of, on lead 147
Waters, detection of lead in 148
Water, distilled 410

Xanthine, behaviour of, with reagents . . . 323
„ composition of 323
„ detection of 323
„ in calculi 336
„ properties of 323

Zinc as reagent 409
„ properties of 45, 51
Zincic chloride, properties of 47
„ compounds, blowpipe tests for 52
„ „ characteristic tests for . . . 52
„ „ flame reactions 52
„ „ properties of 52
„ „ special tests for 52
„ nitrate, properties of 48
„ oxide, „ 46
„ salts, „ 49
„ sulphate, „ 48
„ sulphide, „ 47

Works by the same Author.

THE SECOND STEP IN CHEMISTRY;

OR,

THE STUDENT'S GUIDE TO THE HIGHER BRANCHES OF THE SCIENCE.

Illustrated with numerous Engravings on Wood. Cloth, 10*s*.

"At the meeting of the Cavendish Society, Professor Graham, the President of the Society, said that he considered its mission nearly fulfilled. When the publication of Gmelin's 'Chemistry' was completed, the Society would have accomplished all that could be expected of it. Societies like the Cavendish, in the present day, could not be expected to compete with private enterprise, which now engaged in publications such as would not have been undertaken at the time the Society was commenced. As an illustration, he might mention Galloway's 'Second Step in Chemistry,' a work comparable to the volume of memoirs published by the Society, and which would not have been undertaken by a private publisher sixteen years ago. The Society had, in fact, been superseded by the press, and was no longer called for."—*Chemical News.*

"The success which attended Mr. Galloway's former works has led him to this 'Second Step,' which is indeed a great advance upon its precursors. It is intended to teach the higher branches of the science, especially those newer views, which are now being very generally adopted. We do not know another work in which will be found so clear an exposition of the hypotheses of Brodie, Gibbs, and Odling on molecular constitution. The numerical relations of equivalent numbers and the binary theory of salts are carefully explained. The chapter in which our author deals with the involved but interesting subject of pseudo-morphism and the curious behaviour of crystalline bodies under varying conditions, is an especially satisfactory one. Mr. Galloway deals largely with the vexed questions of the constitution of compound bodies, and examines all the views deserving of notice which have been promulgated by modern chemists. The laws of diffusion, of dialysis, and of osmose—which have been so elaborately worked out by the Master of the Mint (Prof. Graham)—are carefully explained, and the beautiful and fertile field of inquiry which has been opened out by Miller, Kirchoff, Bunsen and others—through the agency of spectrum analysis—is well described. The student who desires to make

the step from the mere mechanics of chemistry to its higher philosophies, will do well to study this volume with close attention."—*The Athenæum.*

"This work is intended to teach the higher branches of chemical science, especially the newer views which are now being very generally adopted, and will be found a most efficient manual for the purpose. To criticise the matter of the book is impossible, since it would involve a criticism on all the views on the constitution of bodies which have been put forward by Griffin, Gerhardt, Williamson, Wurtz, Playfair, Frankland, Kolbe, and others. The arrangement of the matter deserves great praise. Mr. Galloway is a practised teacher of chemistry, and he states from experience that the difficult subjects of which the book treats can be taught with perfect success on the plan here developed. We have no doubt of this, and firmly believe that the student who goes conscientiously through the book, performing all the exercises which are given, will find himself, when he gets to the end, an accomplished theoretical chemist.

"Practical points, however, are not altogether neglected; and much useful information will be found, particularly on fractional distillations, and the method of determining the boiling-points of liquids, &c.

"Mr. Galloway has supplied a want which we know has long been felt by the constant inquiries we have had for a work treating of recent theories, and we have great pleasure in recommending the book to our readers."—*Chemical News.*

"This book is intended for the use of the student of chemistry after he has become sufficiently acquainted with the elementary matters treated of by Mr. Galloway in his 'First Step in Chemistry.' In it are placed before the learner the chief theories and discoveries having a general bearing on chemistry, that have of late been attracting attention in the chemical world. . . . . Without attempting to give any further analysis of this work or any of its chapters, we will only say that the chemical student will find in it as complete an account as he can possibly require of all the subjects of which a list has been given above. The book is, it will of course be understood, not intended as a complete guide in the operations of the laboratory; this duty is left to be performed by such works as those of Fresenius, or Mr. Galloway's own 'Manual of Qualitative Analysis;' but, while the author has necessarily introduced a certain amount of instruction as to the preparation or analysis of various compounds, his main purpose is to place before the more advanced student the abstract principles of modern chemical science. . . . . To increase the utility of this work to the teacher and to the student, Mr. Galloway has in his 'First Step' introduced a large number of *exercises*, which, he believes (and in our opinion rightly), will facilitate the understanding of the subjects. . . . . To those of our readers who have the inclination and opportunity to become acquainted with the principal views of modern chemical philosophy

Mr. Galloway's 'Second Step in Chemistry,' containing, as it does, a full and impartial exposition of the various doctrines and discoveries, will be a most valuable guide."—*British Medical Journal.*

"Mr. Galloway has already on two several occasions earned the thanks of both teachers and students by his 'First Step' and his 'Manual of Qualitative Analysis.' In the former of these works he has expressed and carried out his opinion that chemistry, to be taught successfully, must be taught like arithmetic. How correct this theory is has been well shown by the success of the work itself, now the pioneer of the science in many educational establishments throughout the kingdom. It is on a precisely similar plan that the book under consideration has been constructed. In it the object of the author has been to lead the student from the simpler facts and theories of the science to its more advanced and more complex developments, and to explain those views of modern chemists which are day by day becoming more generally adopted. . . . . Having thus given a very incomplete sketch of the general plan of the work, it remains for us to notice some points of peculiar excellence in its construction, and some in which it differs entirely, or rather which separate it entirely in character, from all other manuals of the science. Firstly, as regards the exercises which, at the conclusion of each chapter, the student is required to perform. This system of exercises is one of the most important features of Mr. Galloway's plan, and is mainly that by which he assimilates his method of teaching to that employed in teaching arithmetic. . . . . These exercises on organic chemistry are perfectly new, and we believe we are correct in stating that this branch of the science has never before been attempted to be taught on such a system. Of the certainty of its success we can have no doubt.

"Mr. Galloway has also in this book supplied a want which even the most advanced students of the science frequently find occasion to deplore. We allude to the absence even in the most systematic treatises, of any attempt on the part of the author to present to his readers even an outline of the train of reasoning which has led to the adoption of particular views. In the work under consideration, on the contrary, we have laid before us all the arguments for and against the adoption of each theory, and we need scarcely say how much this is likely to contribute to a clear comprehension of the theory itself. As admirable examples of the feature to which we refer we would cite the chapter on the History and Progress of the New System of Classification, that on the Polyammonias, and the paragraph on Biatomic Organic Acids, page 355, *et seq.*

"A most flattering tribute was the other day parenthetically paid to both the author and publisher of this manual. At the anniversary meeting of the Cavendish Society Professor Graham, its president, who occupied the chair, said that he considered the mission of the Society nearly fulfilled. Societies like the Cavendish could now no longer compete with private enterprise. Professor Graham mentioned in illustration Galloway's 'Second Step in Chemistry,' 'a work comparable to the volume of memoirs published by the Society, and which would not have been undertaken by a private publisher sixteen years ago.' Mr. Churchill at least must feel gratified by the official announcement that he has in this work afforded evidence that 'the Society had, in fact, been superseded by the press, and was no longer called for.' Mr. Galloway, we would say in conclusion, deserves, and will doubtless obtain, the thanks, not only of every student of the more advanced branches of chemistry, but of every chemist who desires to see his science taught as something more than either a mere ill-arranged collection of heterogeneous facts, or as a tissue of mysticism and idle speculation. He has already established a claim to be considered a lucid teacher of its simple principles; he will now, as this book wins its way to the centres of scientific education, be recognised as one of the ablest exponents of its higher truths."—*Dublin Medical Press.*

"The author has spared himself no amount of labour in bringing out this 'Second Step;' and it may with safety be averred that the result reflects equal credit on him as a thoroughly well-read chemist and an able exponent of the subject which he professes to teach. This text-book may be said to embody everything that is at present known regarding philosophic chemistry; and while it contains all that concerns the theoretical branches of the science, it is also adapted for employment as a book of reference by those pursuing a series of practical organic investigations. The views of all the modern English and Continental chemists find a place in Mr. Galloway's manual, so that the student is not treated to an author's hobby, but has the option of selecting those opinions which appear to be supported by the greatest weight of evidence. The laws regulating the constitution of bodies are concisely stated; their history and progressive development being described at some length, the writer beginning with the discoveries of Clarke and Griffin, and terminating with those of Gerhardt, Laurent, Williamson, Frankland, Kolbe, and others. Exercises to be worked out by the reader are scattered through the text, and the appendix contains a useful list of questions given by various examining boards. We trust Mr. Galloway's hand-book may meet with the encouragement it deserves; it commends itself to every serious student of chemistry."—*Popular Science Review.*

"This is a book with a thousand virtues and only one fault. Judge of our surprise when, wishing to refer to certain pet subjects as tests of its excellence, we found that there was actually no 'Index.' No second edition—and we have every reason to feel sure that there will be a necessity for one very soon—should be allowed to appear without this very necessary adjunct to a standard scientific work. Having now made a clean breast of the matter and said *all* we are compelled to say in its dispraise, we commence the more pleasing task of giving our readers a notion of the various excellencies of Professor Galloway's production. First of all, it supplies the great chemical want of the present day, and forms a stepping-stone between the old and new schools of chemical philosophy. The adherents to the new school are constantly advising their conservative friends to join them, but the answer of the latter is always to the effect that there is no work in the English language which would give them a history of the steps by which the new theories had been arrived at. It is, therefore, with the greatest delight that we hail the appearance of Professor Galloway's 'Second Step,' giving as it does a complete history of the rise and progress of the unitary system. The labour gone through must have been enormous, for Mr. Galloway appears to have ransacked the scientific publications of every country for the last thirty years for every paper that could in any way bear on the subject.

"We look on the appearance of this book as an important step in advance—the most important that has been made since the issue of the first part of Odling's Manual, and one which will do much to spread the truths of the unitary system. A short time since, when we gave our readers an account of Dr. Apjohn's 'Manual of the Metalloids,' in which we regretted that the learned doctor had not thought proper to adopt the new system, we had no idea that we should so soon have the satisfaction of seeing a work like the present from the hands of another Dublin professor. . . . . . We congratulate the former institution (Museum of Irish Industry) on producing so necessary and excellent an addition to our standard scientific literature. We cordially recommend the 'Second Step' to all our readers—to the followers of the old school, in order that they may understand the new theories, even if they should be too conservative to adopt them; and to students, that they may commence the acquisition of chemical knowledge by the best text-book of the new system, which must eventually supersede the old one."—*The Chemist and Druggist.*

"In all this a direct appeal is made to the exercise on his own part of the student's reasoning powers, and at the same time he has afforded him an amount of assistance not incompatible with a healthy development of his intellectual faculties. We need scarcely add that we most heartily wish Mr. Galloway's valuable and masterly treatise all the success it so honestly deserves."—*Dublin Quarterly Journal of Medical Science.*

THE FIRST STEP IN CHEMISTRY.

A NEW METHOD FOR TEACHING THE ELEMENTS OF THE SCIENCE.

Fourth Edition, Illustrated with Engravings on Wood; foolscap 8vo, cloth, 6s. 6d.

"Beginners in the study of chemistry are much indebted to Mr. Galloway, for the great pains he has taken in the book before us ('Manual of Qualitative Analysis'), and in his 'First Step in Chemistry,' to remove from the path of the student the many difficulties and obstacles which hinder his early progress. These difficulties, so puzzling and discouraging to the pupil, are too often forgotten or neglected by the compilers of such text-books; but our author has evidently devoted considerable and especial attention to them, and we think he has been successful in most materially facilitating the acquisition of sound knowledge in the first stages of chemical study."—*Philosophical Magazine.*

"We spoke favorably of Mr. Galloway's work on 'Qualitative Analysis,' and we are no less pleased with his 'First Step.'"—*Athenæum.*

"Nobody, we presume, who desired to learn a foreign language would begin with the hopeless task of committing to memory the pages of a dictionary. But this is precisely the course which students were obliged to take in chemistry previous to the appearance of Professor Galloway's text-books in that science. Mr. Galloway's 'First Step' is a Grammar and Exercise Book combined. It does for the learner in chemistry just what such a book as Smith's 'Principia Latina' does for him in Latin, or what Euclid did for the school-boys of two thousand years ago in geometry. Examine any one of the thousand and one Elements of Chemistry, Manuals of Chemistry, &c., which pour in such profusion from the press, and you will find that they are all constructed on the dictionary principle. They are books of reference. The elements are classified and enumerated, and the properties of each, in its various combinations, more or less copiously enumerated. A text-book of this sort has its utility, but the utility is not for a beginner. The book serves as a book of reference for those who have already acquired a moderate knowledge of the subject, and who have occasion to revive or to extend that knowledge from time to time. In departing from this beaten track and in recognising that chemistry can be taught only by the same methods which have been successful in all the other branches of learning, Mr. Galloway has rendered a most important service to the rising generation, and has brought within the bounds of

possibility that which has hitherto appeared nearly hopeless, the introduction of chemistry into the curricula of school and college education."—*Irish Times.*

"We have thus glanced at the principal features of Mr. Galloway's system of instruction, and although, as the book has now reached a third edition, it is pretty extensively known, we have done so, because we believe that the principles of such a system cannot be too widely diffused, and that, if universally employed, not only would the beginner be spared much disappointment, but many more really practical chemists would be given to science. We have marked several portions of Mr. Galloway's book, the peculiar merits of which, did space permit, we should notice at length, but we think that our readers will, from the above *résumé*, get an idea of its general plan, and for its details we refer them to the book itself. We cannot, however, conclude this notice without reference to the chapter on the atomic theory, and that on isomerism, as examples of that clearness of explanation which is pre-eminently the characteristic of the whole work. Of the manner in which a subject may be treated, so as to combine interesting reading with sound instruction in confessedly difficult subjects, the sections on light and electricity may be cited as illustrations.

"In conclusion, we confidently recommend this little book to all who seek an introduction to chemistry, as a book which will, if properly studied, leave them in an infinitely better position than years of attendance upon lectures on the science, and with a practical knowledge of all its fundamental truths."—*Dublin Medical Press.*

"We heartily commend this unpretending work to the heads of scholastic establishments, and to others who are anxious to initiate their pupils into the principles of a most fascinating and most useful branch of human knowledge."—*London Journal of Medicine.*

"The author of this manual complains, and with some justice, that the elementary works on the science of chemistry do not begin at the beginning, and, consequently, do not follow up the various stages in their natural and proper order. Chemistry should be taught as arithmetic. . . . . This is the plan pursued by Mr. Galloway, and the arrangement of the subject is one of the distinctive features of his book. But besides this, he lays great stress on instruction in working examples; to lay down rules simply would utterly fail as a method of teaching chemistry, just as much as it would fail in arithmetic. The exercises in this book are most abundant, and constitute its second recommendation. On the whole, we think it a very excellent work, and we recommend it to the notice of our readers."—*English Journal of Education.*

"This method of instruction seems likely to meet with considerable success in schools and other establishments, where a study of chemistry is not a chief branch of education, but must take its place by the side of Latin and Greek; and, as such, it gives us pleasure in being able to cordially recommend this useful little book."—*Chemical News.*

"We have seldom had an opportunity of witnessing so large an amount of valuable information compressed in so small a space; and to the young student in chemistry, as well as the more matured one, we have no hesitation in strongly recommending the result of Mr. Galloway's labours."—*Morning Herald.*

"The plan of teaching adopted by Mr. Galloway differs very considerably from the plans hitherto laid down; and the fact of a second edition of the work having been called for is a proof that Mr. Galloway's system is highly appreciated by the public. . . . . For interest and perspicuity, this is the most complete elementary treatise on chemistry which has yet appeared; and we can confidently recommend its study to all those who wish to become acquainted with that valuable science."—*Morning Chronicle.*

"Enough has been said to show the scope and design of Mr. Galloway's 'First Step in Chemistry.' We recommend it to every beginner in the study of that science, as better fitted to smooth his first difficulties than any other work with which we are acquainted."—*Morning Post.*

'We have been waiting with interest the promised new edition (4th) of Professor Galloway's 'First Step in Chemistry,' and are pleased to announce that it has just appeared, re-written, greatly enlarged, and much improved. We remember the first edition of this book, very thin and unpretending, but very practical and easy to understand; introducing students and young people to an accurate knowledge of the *alphabet* of a fascinating science, and leading them on by easy gradations until they could spell out for themselves some of its most important lessons. Then came the second edition, thicker and more complete, then a third still thicker; and now, after being out of print for many months, we welcome the fourth, which has become quite a thick little manual of 470 pages small 8vo, and contains the new nomenclature, besides many other additions —the result of the author's experience in teaching. Whenever we are asked to recommend a book on chemistry to a beginner, we never fail to mention Galloway's 'First Step,' and if this science is to be taught in schools this is the manual which the pupils should adopt as their guide. We have known rapid progress made by those who have confined themselves to this one book, and no one of average intelligence would follow the author's instructions without laying a broad foundation of knowledge upon which he might go on building with ease and confidence. Professor Galloway's method can scarcely be called new any longer, for it has stood the test of experience, and is thoroughly established in public favour. As arithmetic cannot be taught by lectures alone, but requires the pupil himself to perform the operations of addition, subtraction, multiplication, and division, so Mr. Galloway expects the student to go through a series of exercises as important to a practical acquaintance with chemistry as the first four rules are to those who would comprehend arithmetical calculations. The nomenclature and notation of chemistry, the use of signs and brackets, the construction of formulæ, the mode of expressing chemical changes, the method of determining the quantities of the constituents in given quantities of compounds, and other equally valuable processes, form the subjects of numerous exercises, which are so gradually progressive as to advance the student by almost imperceptible degrees from the darkness of total ignorance to familiarity with the great principles of the science. This is the way we learn to read, first the alphabet, then simple syllables, then words of one, two, or three syllables, which we learn to spell for ourselves, and to combine with each other. The method is a thousand times more easy and more effectual than a study of each of the elements with all its combinations in succession, which leaves the last lesson nearly as difficult to acquire as the first. The 'First Step' must, therefore, continue to enjoy the favour that was shown to former editions as an excellent plan of teaching chemistry to the young. Medical students would do well to begin with it. Schools that teach chemistry will be sure to give it the preference. Popular classes everywhere will employ it. Students who have no teachers can procure no better work, and the book must have a still wider field; for the number of those interested in chemical processes as manufacturers is constantly increasing, and we would advise them, if they have embarked their money in such things without understanding them, by all means to begin with the 'First Step,' and learn what so much concerns them. In any case they would also do well to use all their just influence over those they employ, to encourage them also to the same course."—*Medical Press and Circular.*

Price 2s. 6d.

A KEY,

Containing Answers to the Questions in the Fourth Edition of
'The First Step in Chemistry.'

'The First Step in Chemistry,' 'The Second Step in Chemistry,' and *'The Manual of Qualitative Analysis,'* are recommended by the Committee of Privy Council on Education, as Text-books for the Examinations of the Department of Science and Art.

CHEMICAL TABLES.

FOUR LARGE SHEETS, FOR SCHOOLS AND LECTURE ROOMS.

SECOND EDITION. PRICE 4s. 6d. THE SET.

1. TABLE OF ELEMENTS. WITH THEIR SYMBOLS, ATOMIC WEIGHTS, AND SPECIFIC GRAVITIES.
2. TABLE OF BASES, WITH THEIR SYMBOLS AND COLOUR.
3. TABLE OF ACIDS, WITH THEIR SYMBOLS, AND THE STATE IN WHICH THEY EXIST.
4. TABLE OF THE GENERAL FORMULÆ OF SALTS.

These Tables and the 'First Step,' are placed on the List of School Books of the Educational Committee of the Privy Council

---

"These tables are intended for schools and lecture-rooms, being printed on five large sheets, in characters so bold and distinct that they may be distinguished at a considerable distance. The first, which covers two sheets, is a Table of the Elements, giving the names of all the different metalloids and metals, the chemical symbols, the atomic weights, and the specific gravities. The names of the rare elements are printed in italics. The second table gives the names, colours, and symbols of the various basic substances; the third, the names, properties, and symbols of the more important acids; and the fourth exhibits the general formulæ of the more important salts. These tables ought to be affixed to the walls of every school-room in which the natural sciences are taught, and they would certainly not be out of place on the walls of any pharmaceutical laboratory. Lecturers on chemistry may feel particularly obliged to the excellent chemist of the Dublin Industrial Museum, for having saved them a vast expenditure of Indian-ink, time, and trouble."—*Chemist and Druggist.*

This book should be returned to the Library on or before the last date stamped below.

A fine of five cents a day is incurred by retaining it beyond the specified time.

Please return promptly.

MAY [illegible]

[illegible] 14 1926

[illegible]

Chem 668.70.2
Manual of qualitative analysis,
Cabot Science 001462420
3 2044 091 983 098